

July, 1930

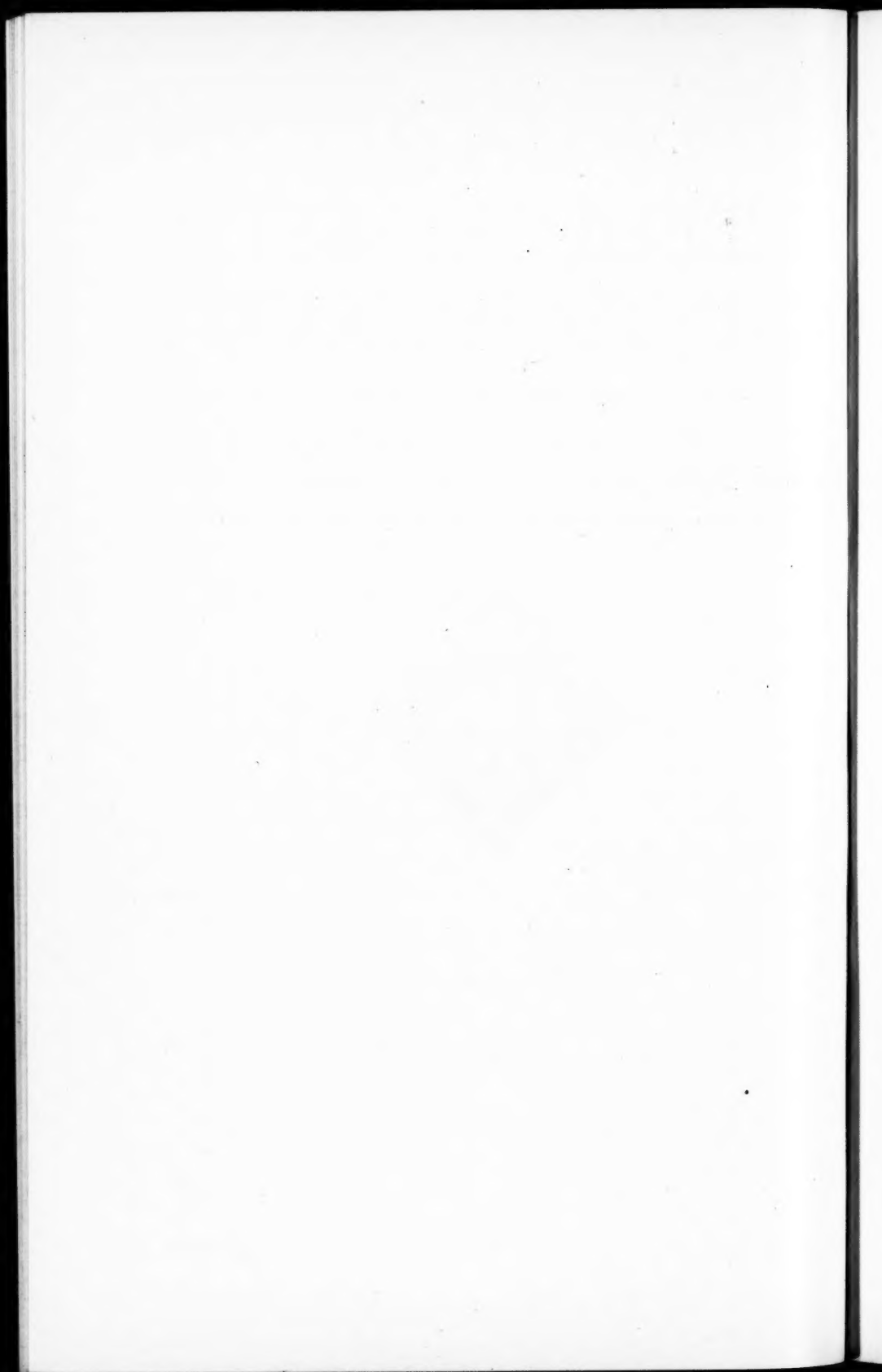
RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME III

NUMBER 3



RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor.....C. C. DAVIS
Associate Editor.....H. L. FISHER
Secretary-Treasurer.....H. E. SIMMONS

Vol. III

July, 1930

No. 3

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

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Vice-Chairman.....H. E. WINKELMANN, Philadelphia Rubber Works Co.
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
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THOMAS M. KNOWLAND, *Secretary-Treasurer*, 76 Bradford Rd., Watertown, Mass.

Entire membership..... 721

Members.....	460	
Associate members.....	159	
Subscriptions.....	73	
Honorary members.....	29	721

Members paid for 1930.....	367	
Ass't members paid for 1930.....	96	463

Members in arrears for 1930.....	93	
Ass't members in arrears for '30..	63	156

Subscriptions paid for 1930.....	62	
Subscriptions unpaid for 1930....	11	73
		692

H. E. SIMMONS, *Secretary-Treasurer*

General Spring Meeting of 1930

The General Meeting of the Rubber Division was called to order in the Social Rooms of the First Baptist Church in Atlanta, April 9.

There were 107 in attendance at the opening of the session.

A short business meeting was held, at which time the changes in the Papers Committee Report, as recommended by H. L. Fisher and approved by the Executive Committee, were placed before the Division. After a short discussion the rules as proposed were adopted, the new rules to govern the preparation and presentation of the papers in the future:

1. That two copies of each paper be in the hands of the Secretary six weeks prior to the meeting.
2. That the author send in an abstract of not over two hundred words along with his manuscript.
3. That the Chairman appoint two or three men to act as reviewers for each paper presented to the division, and to lead in the discussion of the paper.
4. That the reviewers submit their comments in duplicate without signatures, and that the secretary send one anonymous copy of each to the author of the paper. The author may use these comments in rewriting his paper, but he may not expand it beyond its original scope. The final paper for publication must be in the hands of the Secretary before it is presented at the meeting.
5. That the discussion of papers be reported as far as practicable and be published in concise form, but that the discussion not be published until after it has been revised by the authors of the discussion.
6. That the authors and the reviewers give the secretary the number of minutes to be allotted on the program for the paper, and that the author be notified of the time allotted to him.
7. That a paper should usually consist of the following parts:
 - (a) Synopsis
 - (b) Brief introduction
 - (c) Main body, including experimental work
 - (d) Conclusions
 - (e) Bibliography
8. That, in the presentation at a meeting, the author should never read his complete paper. He should use a comprehensive abridgment, and carefully think over his method of presentation beforehand. Properly made slides or charts are most helpful and, when discussing them, the speaker should talk to the audience, not to the screen.
9. That the original and two extra copies of the drawings or data from which slides are to be prepared shall accompany the paper, and that the author should observe the following in the make-up of the slides:
 - (a) Too much should not be put on one slide
 - (b) All curves should be distinctly drawn
 - (c) Letters and figures should be large enough when on the screen to be legible from the rear of a 100-ft. room
 - (d) Slides should be numbered
10. That charts, curves, and tables for publication should conform with the recommendation on these matters given in the article in *Industrial and Engineering Chemistry*, 19, 755 (June, 1927); and that bibliographies should conform with the standard practice of the Society publications.

Authors are reminded of the fact that, in the American Chemical Society publica-

tions, the metric system of units must be used, and that the English system may be used in addition.

Committee on Papers,

C. R. BOGGS
H. E. SIMMONS
A. A. SOMERVILLE
W. B. WIEGAND
H. L. FISHER, *Chairman*

A. A. Somerville, Chairman of the Physical Testing Committee, made a short report of the work which had been done, and called our attention to the fact that the work had been discontinued, due to the withdrawal of the financial support of the Rubber Manufacturers Association. Upon motion his report was accepted and a resolution was adopted to authorize the Chairman to appoint a committee who would approach the officers of the Rubber Manufacturers Association in an effort to interest them again in taking up the work of the Physical Testing research. Committee appointed was Stanley Krall, W. A. Gibbons, and W. L. Sturtevant.

The Chairman then appointed a Resolutions Committee of R. P. Dinsmore, C. W. Bedford, and E. C. Zimmerman. Following this the program of the Division was carried out as follows:

First Morning

1. A. A. Somerville. Report of the Physical Testing Committee.
2. A. A. Somerville, J. M. Ball, and L. A. Edland. "Autographic Stress-Strain Curves of Rubber at Low Elongations."
3. Ernst A. Grenquist. "Structural Changes during Processing of Rubber."
4. John T. Blake. "Thermochemistry of Vulcanization of Rubber."
5. John T. Blake. "Kinetics of Vulcanization of Rubber with Sulfur and Selenium."
6. John T. Blake. "Vulcanization of Rubber with Nitro Compounds."
7. C. R. Boggs and J. T. Blake. "A Theory of Vulcanization of Rubber."

First Afternoon

8. W. L. Semon, A. W. Sloan, and David Craig. "The Surface Application of Age Resisters to Cured Rubber vs. Mill Incorporation Prior to Cure."
9. J. W. Temple, Sidney M. Cadwell, and Morris W. Mead, Jr. "Early Stages of Oxidation in Rubber—A Quantitative Application of the Pyrrole Test."
10. Ira Williams and Arthur M. Neal. "The Solubility of Oxygen in Rubber and Its Effect on the Rate of Oxidation."
11. Harry L. Fisher and F. D. Chittenden. "3-Methyl-1,3-Pentadiene."
12. B. W. Rowland. "Some Aspects of Double Refraction and Structure in Rubber."

Second Morning

13. C. R. Park. "The Effect of Curing Temperature upon the Properties of a Rubber-Sulfur Mix."
14. W. F. Busse and W. B. Doggett. "Application of the Falling Cylinder to the Measurement of the Viscosity of Thick Rubber Cements."
15. S. C. Nicol. "The Moisture Content of Crude Rubber and Its Effect on Modulus of Cured Stock."
16. Raymond P. Allen. "A Method of Making Micro-Sections of Rubber Stocks."
17. H. A. Winkelmann and E. G. Croakman. "The Behavior of Various Clays in Crude and Reclaimed Rubber."

18. W. B. Wiegand and C. R. Boggs. "Carbon Black in Rubber Insulating Compounds."
19. W. S. Conover. "The Effect of Pigmentation on the Work of Retraction of Rubber Compounds."

At the close of the official program, E. C. Zimmerman made a report of the Resolutions Committee as follows:

"Your Committee on resolutions recommends that the following resolutions be presented to the Atlanta section of the American Chemical Society and the Atlanta Chamber of Commerce:

WHEREAS, it has been the good fortune of the Rubber Division of the American Chemical Society to enjoy the true southern hospitality of the city of Atlanta, and the Atlanta Section of the American Chemical Society.

AND WHEREAS, we have been inspired by the Georgian sunshine.

AND WHEREAS, we have regaled our appetites with many tasty examples of southern epicurian art.

AND WHEREAS, the entertainment of the visiting chemists has been noteworthy for the tasteful decorations, expeditious registration, enjoyable bar-beque, and educational trips.

AND WHEREAS, we appreciate that all of this has been made possible by the sacrifice of much time and expense by the city of Atlanta;

BE IT THEREFORE RESOLVED, that appreciation of the Rubber Division of the American Chemical Society be conveyed to the Atlanta Section and to the Atlanta Chamber of Commerce, and through them to all other agencies who have contributed to the success of the meeting.

BE IT FURTHER RESOLVED, that this resolution be spread on the records of the Rubber Division of the American Chemical Society."

which upon motion was accepted.

The Secretary-Treasurer then submitted the following report which upon motion was accepted and ordered placed on file:

Meeting of the Executive Committee, on April 9, with the following members present: Ira Williams, Harold Gray, H. A. Winkelmann, L. B. Sebrell, Stanley Krall, H. E. Simmons.

Harry L. Fisher, Chairman of the Papers Committee, appeared before the Executive Committee and made certain recommendations for changes in the previous reports of the Papers Committee. By motion these changes were approved and referred to the Division for their consideration.

By motion the Secretary was authorized to correspond with W. F. V. Cox, Secretary of the Institution of the Rubber Industry, extending to their members an invitation to attend the 1932 Fall Meeting of the Rubber Division.

The suggestion made by H. E. Howe that the Rubber Division publish a Monograph on Rubber was brought to the attention of the Executive Committee, and after a short discussion L. B. Sebrell and H. E. Simmons were appointed a Committee to go over this question with the idea of laying out a program to the end that such a Monograph might be prepared.

The Chairman appointed J. M. Bierer, R. P. Dinsmore, and A. A. Somerville as a Committee of three to make whatever arrangements are necessary in connection with a joint conference which will be held in England during May and June of 1931.

Upon motion the Committee adjourned to meet again at the call of the President.

H. E. SIMMONS, *Secretary-Treasurer*

Local Group Activities

Akron Group

May 12, 1930. Address by L. V. Cooper (Firestone Tire & Rubber Co.) on "Laboratory Evaluation of Flex Cracking Resistance," by J. D. Morron (Mechanical Rubber Co.) on "Applications of Modern Statistical Machinery to Rubber Compounding," by Joseph Torrey, Jr. (Goodyear Tire & Rubber Co.) on "Quality Control in Tire Manufacture," by Henry Schippel (Goodrich Co.) on "Airplane Tires and Wheels," by J. P. Maider (Goodyear Tire & Rubber Co.) on "Cleaning Rubber by the Strainer Method," and by F. L. Haushalter (Goodrich Co.) on "Field Application and Cure of Rubber Lining to Ball Mill."

Chicago Group

March 21, 1930. Addresses by C. F. Schnuck (Farrel-Birmingham Co.) on "Roll Mills and Banbury Mixers," and by H. A. Depew (New Jersey Zinc Co.) on "The Behavior of Pigments during Mixing and Curing."

Los Angeles Group

February 26, 1930. Joint meeting with the Southern California Section of the American Chemical Society. Addresses by H. E. Howe on "Alcohols, New and Old," and by F. W. Stavely, on "The Rubber Industry of Los Angeles."

April 25, 1930. Addresses by R. R. Jones (Firestone Tire & Rubber Co.) on "Industrial Power," and H. R. Lamberth (Fluor Construction Co., Los Angeles) on "Atmospheric Water Cooling."

New York Group

March 28, 1930. Addresses by B. H. Foster (U. S. Rubber Co.) on "Getting Better Acquainted with the Stretch Property of Cotton," and by E. G. Holt (U. S. Department of Commerce) on "Crude Rubber Statistics."

May 22, 1930. Addresses by J. N. Kuznick (Manhattan Rubber Mfg. Div. of Raybestos-Manhattan, Inc.) on "Rubber in the Grinding Wheel Industry," by D. E. Jones (American Hard Rubber Co.) on "Hard Rubber and Some of Its Unusual Applications," and an informal talk by W. C. Geer on work to prevent or remove ice on airplane wings, work which is being carried on at Cornell University.

Report of the Treasurer of the Rubber Division

Last Treasurer's report, 3/19/30—balance in bank.....	\$1545.84	
Deposits—dues.....	152.20	\$1698.04
<hr/>		
Expenditures:		
Postage and telegrams.....	\$16.07	
Translations.....	196.21	
Mack Printing Company.....	10.33	
Ben Franklin Printing Co.....	7.00	
Stenographic services.....	30.00	
Expenses of the Sec'y-Treas. to Atlanta meeting.....	83.50	
Refund.....	2.00	
	<hr/>	
Total expenses.....	345.11	
Correction of \$.08 due to foreign checks and drafts.....		\$1697.96
Expenses.....		345.11
		<hr/>
Bank balance as of June 1st.....		\$1352.85

H. E. SIMMONS, *Secretary-Treasurer*

Corrections

In an article in the April issue by T. L. Garner on "Factors in the Works Control of Plasticity by the Williams Method," on page 293, lines 13 and 15, the expression "400-thousandths of an inch" should read "4 millimeters." This correction has already been made in an issue of the *India Rubber Journal* subsequent to the original article.

In the Table of Contents in the April issue, the name A. HEALY should read A. HEALEY. In the title of the article itself on page 271 the name is correct.

New Books and Other Publications

Bibliography on Rubber Technology, 1924-1925. Section I, Latex and Raw Rubber. Compiled by Edith L. Shearer for the Technical-Commercial Group Special Libraries Association. 1930. Multigraphed pamphlet, 14 pages, 8½ by 11 inches.

This publication is Section I completing, with former issues, a volume of bibliography on rubber technology, the earlier parts of which from 2 to 7 inclusive were issued in 1926. This section covers the literature on latex and raw rubber for 1924 and 1925, both papers and patents. Copies of this list can be obtained by addressing E. L. Shearer, Room 2008, 195 Broadway, New York, N. Y. [From *India Rubber World*.]

The Chemistry of Rubber. By Harry L. Fisher. Reprinted from *Chemical Review*, Vol. VII, No. 1, March, 1930. 88 pp.

Dr. Fisher has divided this study into three parts, the first dealing with latex and crude rubber and the second with the rubber hydrocarbon, its structure and properties. The major portion of the study, however, is devoted to his third topic of chemical reactions and derivatives. While not attempting to cover exhaustively all the theories of vulcanization and rubber technology, Dr. Fisher's work reviews the principal research done up to date and is rounded out by copious references. [From *The Rubber Age* of New York.]

Latex, Its Occurrence, Collection, Properties, and Technical Applications. By Ernst A. Hauser, with patent review compiled by Carl Boehm Von Poernegg. Translated by W. J. Kelly. Book Dept., The Chemical Catalog Co., Inc., 419 Fourth Ave., New York, N. Y., 1930. Cloth, 201 pages, 6 by 9 inches. Indexed, illustrated.

Hauser, who is recognized as an outstanding authority on rubber latex, has assembled in this volume a general review of the known facts regarding Hevea latex and of the less important gutta-percha and balata trees.

Following an historical introduction, the author discusses latex collection, its physical and chemical properties, non-rubber constituents, coagulation, and preparation of "whole latex rubber." The technology of latex is treated at length dealing with its preservation, shipment, concentration, vulcanization, and industrial application. The concluding chapter is a treatise on the internal structure of rubber based on the researches of many scientists who have studied that problem.

An appendix of English and German patent literature arranged chronologically from 1791 to 1927 completes the volume. The book contains author and subject indexes, and throughout is replete with references to scientific and technical literature. The author has been successful in his attempt to fill a distinct need on the part of rubber chemists and technologists for a monograph on rubber latex. [From *India Rubber World*.]

Handbuch der Kautschukwissenschaft. In collaboration: By L. Hock, University of Giessen; E. Kindscher, Division Manager, State Bureau for Testing Materials; A. Koch, I. G. Farbenindustrie A.-G.; H. Pohle, formerly chemist of Continental Caoutchouc und Gutta-Percha Co., Hannover; R. Pummerer, Director of the Chemical Laboratory, University of Erlangen; A. Schob, Division Manager, State Bureau for Testing Materials; A. Zimmermann, formerly Director of the Imperial Institute of Biology and Agriculture, Amani, German East Africa. Edited by K. Memmler, Director, State Bureau for Testing Materials. Published by S. Hirzel, Leipzig, Cl.,

Germany. Cloth, 790 pages, large 8°, 246 illustrations, including 10 plates, in black and colors.

This imposing volume represents the first attempt at a comprehensive work embracing the entire field of rubber science and giving an accurate survey of the present state of research, knowledge, and experience in all its branches. Besides an introduction, the book is divided into seven parts, each part from the hand of an expert in the particular field covered. Part 1. A. Zimmermann. A history of crude rubber including the botany, production, cultivation, and preparation of rubber; individual characteristics of rubber particles in various plants; direct use of latex, liquid or concentrated; coagulation and preparation of latex; effect of storage on rubber. Part 2. R. Pummerer and A. Koch. Chemistry and synthesis of rubber, vulcanization, accelerators, Peachey process, vulcanization with nitro combinations and peroxides, with selenium, selenium chloride, and sulfur rhodanide. Parts 3 and 4. Kindscher. Physical vulcanization and chemical analytical methods. Part 5. L. Hock. Physics of rubber. Part 6. K. Memmler and A. Schob. Mechanical testing methods, covering determination of plasticity, apparatus employed, aging tests, testing of rubberized materials, insulated wires, hard rubber. Part 7. H. Pohle. Technical vulcanizates via the microscope. Not a little is added to the value of this important work by the very large number of fine illustrations in black and in colors which accompany the text. [From *India Rubber World*.]

Annual Survey of American Chemistry. Vol. IV. July 1, 1928, to December 31, 1929. Prepared under the Auspices of the Division of Chemistry and Chemical Technology, National Research Council, James E. Mills, Chairman. Edited by Clarence J. West, Director, Research Information Service National Research Council. Published for National Research Council by The Chemical Catalog Co., Inc., 419 Fourth Ave., New York, N. Y., 1930. Cloth, 549 pages, 5 by 8¼ inches. Author index.

In this annual publication 51 specialists in chemistry and chemical technology contribute to present a complete condensed review of American chemistry for the period from July 1, 1928, to December 31, 1929.

The review of rubber chemistry is by Harry L. Fisher, research chemist, United States Rubber Co., in a chapter outlining published contributions on rubber chemistry in general, vulcanization, latex and dispersions, accelerators, aging, physical properties, and methods of testing, reclaimed rubber, and manufacturing. [From *India Rubber World*.]

The Improvement of Yield in Hevea Braziliensis. By F. Summers. Published by Kelly & Walsh, Ltd., Singapore, F. M. S. 1930. 12s 6d.

The past decade has seen many efforts toward the improvement of rubber growing, as the steady increase in plantation yield per acre testifies. Summers has had long experience in this field, and his work is authoritative. The introduction of the budding method is described in the first section of the volume, and the following chapters trace the further development of this method and explain it fully. [From *The Rubber Age* of New York.]

Annuaire Technique du Caoutchouc, de la Gutta Percha et des Industries qui s'y Rattachent. Published by A. D. Cillard, 49 Rue des Vinaigriers, Paris, France.

This new volume of the "Encyclopedie du Caoutchouc et des Matieres Plastiques" ("Encyclopedia of Rubber and of Plastic Materials") comprises addresses of those concerns connected with the rubber and plastic industries,

distributed under 400 different heads. Manufacturers' lists, which are separately classified, comprise not only France but Germany, Belgium, Spain, Italy, Great Britain, Canada, the United States, and most of the other foreign countries. There is also a list of nearly 900 technical products with their compositions, properties, and principal uses. [From *India Rubber World*.]

Standards Yearbook, 1930. Published by the National Bureau of Standards, United States Department of Commerce, Washington, D. C. 1930. 306 pp. \$0.75.

A summary of the more important research work done by the Bureau of Standards during the past year is to be found in this annual report. Industrial research accomplished by the bureau included abrasion tests for rubber, a survey of the manufacture of sponge rubber, a report on the properties of rubber floor tile, a study of the deterioration of rubber compounds with oxygen bomb tests, and an investigation of the effects of humidity and temperature upon the stress-strain relation and upon the abrasion resistance of rubber. The Rubber Division of the American Chemical Society coöperated with the bureau and has furnished a research associate to work at the bureau. [From *The Rubber Age of New York*.]

Sixteenth Annual Report. Published by the International Association for Rubber and Other Cultivations in the Netherlands Indies, 5 Nieuwe Doelenstraat, Amsterdam, C., Holland. 1930. 46 pp. For distribution to members.

In addition to detailed statistics on the production of plantation rubber in the Dutch East Indies, this report contains a discussion of local labor problems, taxation, and association activities. At the end of 1929 this association had 200 company members and 64 individual members. Appended to its own report, which is printed in both Dutch and English, is a separate 16-page report of its propaganda department, describing the work of that group in developing the use of rubber pads under rails, rubber paints, rubber as a soling material, rubber flooring, and rubber pavements. [From *The Rubber Age of New York*.]

1930 Yearbook. Published by the Tire & Rim Association, Inc., 1401 Guarantee Title Building, Cleveland, O. 132 pp. For distribution to members.

Not only does this annual include full statistics on the number of rims of every type inspected and approved by the association from 1923 to 1929, but it also carries complete load and inflation tables, diagrams of rim contours, a summary of the rim equipment of all American cars, valve descriptions and drawings, and an appendix on European standards. The roster of the association membership and the constitution and by-laws are also contained in the volume. The 1930 Yearbook is in the same large size that was inaugurated last year and is augmented by memorandum pages and sectional indexes. [From *The Rubber Age of New York*.]

The Future of Rubber. By J. C. G. Kunhardt. Published by the Rubber Shareholders' Section, Institution of the Rubber Industry, 10 Charing Cross, London, England. 1930. 38 pp. 2s 6d.

The author has tackled the rubber situation from a rather novel angle, the main center of his arguments being concerned with the probable depreciation of the existing mature areas. For various reasons this aspect of the situation has not so far been given the consideration it deserves, but it is significant that deterioration of old rubber is already becoming a serious problem in the Dutch East Indies and other districts where restriction of output has not been practiced. The writer's contention is that large tracts of rubber will

go out of existence from now on, and, without being dogmatic on the point, he submits estimates which indicate that consumption before long will overtake production, and he contends that the price of the commodity, as a result, must rise considerably during the next few years. He figures that the world's normal consumptive capacity at 10 per cent. annual increases will exceed the world's normal productive capacity in 1930 by 41,750 tons and by greater amounts yearly until 1935, when consumption will be 505,854 tons higher than production. The author's conclusions will make interesting reading for rubber plantation shareholders. [From *The Rubber Age* of New York.]

Adhesion Problems in Connection with Rubber Flooring. Report of the Rubber Flooring Research Committee of the Propaganda Department of the International Association for Rubber and Other Cultivations in the Netherlands Indies. International Rubber Association, The Hague. 1930. Paper, 151 pages, 6½ by 10 inches. Illustrated. Index.

This comprehensive report is of great interest and importance to all concerned with overcoming the practical difficulties met with in attaching successfully rubber flooring to different sorts of materials used as sub-floors.

Following a brief outline of the problems connected with laying rubber flooring and consideration of adhesion processes in general, the succeeding chapters of the report cover the committees' testing methods and material; adhesion to wood; magnesium oxychloride floors; concrete; sawdust with cement surface screenings; other sub-floor materials. Discussion of these topics is followed by a section on specifications and instructions on installation and maintenance of rubber flooring. The book concludes with final remarks by the committee.

In concluding this admirable report the committee notes that "the crux of the problem appeared to be the construction of sub-floors suitable for the installation of rubber floors" and cites the need of mutual understanding to induce complete coöperation between rubber manufacturers and architects with regard to the application of rubber flooring. [From *India Rubber World*.]

White Sidewalls. Published by E. I. du Pont de Nemours & Company, Wilmington, Del. 1930. 4 pp. For free distribution.

The purpose of this report is to summarize all of the du Pont laboratory work on white sidewall compounds that was conducted during the latter part of 1929, as well as the company's experience with white sidewalls in production during 1929. The discussion is divided into three parts—the sidewall compound itself, compounds for carcass stocks to be used in white sidewall tires, and tread compounds. [From *The Rubber Age* of New York.]

Electric Equipment for Handling Heavy Material. Published by the General Electric Company, Schenectady, N. Y. 1929. 24 pp. For free distribution.

Modern machinery for the handling of bulk material has been developed to meet a general demand for improved methods. From the handling of bulk material manually forty years ago, the demands of industry have grown until today we have fifteen- to twenty-ton buckets that can move a thousand tons per hour. Especially notable is the saving of time and expense through the quick loading and unloading of cars and vessels. This publication describes the electric equipment in general use for this purpose. [From *The Rubber Age* of New York.]

A Survey of the Trade in Manufactured Rubber Goods. Prepared by the Imperial Economic Committee. Published by H. M. Stationery Office, London, England. April, 1930. 120 pp. 6d.

"The rubber industry depends as to 80 per cent. of its output on tires, which find their market in the motor and cycle industry. The prosperity or reverse of the motor industry, therefore, dominates the whole of the rubber manufacturing industry, for not only have variations in the fortunes of the motor industry a direct effect on the demand for rubber, but they cause obvious indirect repercussions upon the remaining rubber industries by their effect on the price of the raw product." Thus the Imperial Economic Committee sums up the present state of rubber manufacturing, but its report contains in addition a review of current trends in the industry and certain recommendations for improved practices. The need for standardization, for example, is strongly urged for greater economies. The progress of scientific control and research work is also discussed, and the erection of tire factories in Great Britain by American, French, and Italian firms since 1927 is termed a "striking development." The committee has performed a useful service in compiling this report, which, while brief, is an adequate summary of the rubber trade throughout the world. [From *The Rubber Age* of New York.]

Crude Rubber is the title of a pocket-size pamphlet of 35 pages issued by H. Hentz & Co., Hanover Square, New York, N. Y. It contains brief sketches of the salient points relating to rubber production and the rubber future's market. The contents consist mostly of pertinent statistics and data on production, consumption, prices, etc., supplemented by statistics on automobile production and gasoline consumption. [From *India Rubber World*.]

Twenty-First Report. Published by the Rubber Growers' Association, Inc., 2 Idol Lane, Eastcheap, London, E. C. 3, England. 1930. 44 pp. For distribution to members.

Included in the Rubber Growers' Association are 612 companies with a combined authorized capital of \$670,000,000, together with 17 other companies not directly owning rubber estates and 439 individuals. It is the spokesman of the great British plantation industry, and its activities, as chronicled in this report, embrace rubber research work, propaganda work for rubber products, and coöperative effort with producers of other countries, such as the current May tapping "holiday." The association now has a propaganda fund of well over \$500,000. In addition to reviewing these activities, the annual report presents financial statements and gives a roster of the membership. [From *The Rubber Age* of New York.]

Rubber and Rubber Shares. Compiled by Gow, Wilson, & Stanton, Ltd., 13 Rood Lane, London, E. C. 3, England. 1930. 2s.

Two features mark this handbook as important to the rubber trade. First, there is set forth a rather ingenious plan for the valuation of rubber plantation company shares, with adjustments for declines or rises in the price per pound of the commodity. Secondly, estimates are made of world requirements of crude rubber from 1929 to 1938, showing a total prospective deficiency of some 1,700,000 tons over the next eight years. These approximations may also be characterized as ingenious, but are still of interest to the industry. [From *The Rubber Age* of New York.]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the April 10 and 20, May 10 and 20, and June 10 and 20, 1930, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Rubber research in Holland. A. VAN ROSSEM. *India Rubber J.* **78**, 630-2 (1929).—The work of the Netherlands Government Rubber Institute is described and illustrated. C. C. DAVIS

The natural coagulation of Hevea latex. A. S. CORBET. Rubber Research Inst. Malaya, *Bull.* No. 1, 15 pp. (1929); *J. Soc. Chem. Ind.* **49**, 36-8T (1930).—A review of the literature shows two opposing theories to explain the cause of natural coagulation, that of enzyme action and that of bacterial activity. In favor of the former are the facts that (1) sterilized latex does not coagulate on standing or with acid, but does on addn. of fresh latex; (2) coagulation is accelerated by Ca salts which favor clotting enzymes but is inhibited by Ca precipitants; and (3) latex coagulation is analogous to that of blood and of milk. In favor of the bacterial activity are the facts that (1) sterile latex and latex sterilized by heat do not coagulate until inoculated; (2) bacteria are found in latex which coagulates, but none in latex which remains liquid; and (3) of the bacteria in latex, 1 species fermented the "carbohydrate" (methyl-*l*-inositol) to an acid and this bacillus is always present. In the present investigation samples of latex of different ages were examd., and in all cases where coagulation had begun, the bacteria content was tremendous. From cultures a predominant bacillus, which was always present, was isolated and studied in detail. It has not been named, so the name *B. pandora* is proposed. It is responsible for most of the important biochem. changes in latex during natural coagulation. It is large (av. 3.1 by 0.9 μ), stains readily with carbol-fuchsin, is Gram-positive, forms spores, is a facultative anaerobe, liquefies gelatin, reduces nitrates to nitrite (without gas), decolorizes litmus, does not form H₂S, does not decomp. starch or cellulose, forms gas from glucose, forms acid and gas from lactose and sucrose, coagulates milk with formation of indole and digests albumin with evolution of NH₃. The *p_H* range of its existence is 4.0 to 10.0. Latex sterilized by heat was coagulated by *B. pandora*, with an acid serum. Latex "carbohydrate" (presumably methyl-*l*-inositol) solns. became acid but did not evolve gas when inoculated. When inoculated with *B. pandora* a mixt. contg. no enzymes flocculated in 2-3 days, but coalescence was slow and incomplete. Similar mixts. with higher concns. of rubber coagulated more readily. Heating latex rapidly to 140-50° in an autoclave does not sterilize it and it coagulates under such conditions. *B. pandora* grew in 0.003-0.2% aq. Na₂SO₃, so the 0.05% Na₂SO₃ recommended by Eaton as an anti-coagulant cannot owe its benefit to its toxicity toward *B. pandora*. Expts. show that dil. lactic acid decomps. Na₂SO₃ with evolution of SO₂. Accumulation of acid in the latex is thus avoided and coagulation cannot occur until all Na₂SO₃ is decompd. The anti-coagulant action of Na₂CO₃ may be explained similarly. Latex contg. 0.5% NH₃ recommended for preservation does not inhibit the growth of *B. pandora*. In such ammoniated latex bacterial action proceeds normally, but the acid is neutralized as fast as formed, so that coagulation is postponed or prevented, depending upon the proportions of NH₃. In aq. ZnSO₄ of 0.06% or more *B. pandora* would not grow, but at concns. below 0.03% growth became increasingly more nearly normal. The results in general show that *B. pandora* decomps. latex substances with formation of acid and consequent sepn. of rubber. Later the proteins are attacked with formation of NH₃, and so the serum becomes acid and the surface layer alk. during natural coagulation. C. C. DAVIS

The preparation of [rubber] mixtures. M. L. P. *Rev. gén. caoutchouc* **6**, No. 57 9-13 (1929); cf. *C. A.* **24**, 1248.—This deals with the curing and testing of control samples on a lab. scale. C. C. DAVIS

Mixers and mixing. What the internal mixer may mean to the [rubber] industry. H. C. YOUNG. *India Rubber J.* 78, 621-6(1929).—An illustrated description of internal mixers, with a discussion of their advantages over the older type of mills. C. C. D.

More about internal mixers. F. H. BANBURY. *India Rubber J.* 79, 125, 128 (1930); cf. preceding abstr. C. C. DAVIS

A study of the vapor-pressure diminution of rubber jellies. PAUL STAMBERGER. *J. Chem. Soc.* 1929, 2318-26.—Though theories have been advanced to show that the swelling pressure (Posnjak, *C. A.* 6, 3346) can be calcd. from the diminution in vapor pressure of solvents in jellies, this diminution has never been directly measured (cf. Katz, *Kolloidchem. Beihefte* 9, 106(1918)). The vapor-pressure diminutions of protein-free rubber, pale crepe, highly masticated rubber purified by soln. in C_6H_6 and pptn. with $AcMe$, and highly masticated plantation rubber in C_6H_6 , in $CHCl_3$ and in CS_2 were detd. Concn. were low so that the results could be compared with the behavior of mol. disperse solns. Detns. were made again after 2 yrs. Two methods were used: (1) that of Gay-Lussac-van Bemmelen and (2) a direct method in a modified Bremer-Frowein tensimeter. All rubbers behaved the same way, and the values were the same after 2 years. Comparison of the relation between the lowering and concn. with that of mol. disperse solns. shows a great difference. Up to a definite concn. there was no lowering, but above this crit. concn. the diminution increased rapidly with the concn. The agreement in results with rubber in different conditions indicates a uniformity in character and not a mixt. of hydrocarbons in different states of polymerization. The results also render very improbable the explanation of Freundlich and Posnjak (cf. *Kolloidchem. Beihefte* 3, 445(1912); cf. *C. A.* 6, 1701), but supports the theory of Katz. The swelling pressures calcd. from the vapor-pressure lowering agreed roughly with the exptl. values of Posnjak. From the qual. behavior of the jellies, *i. e.*, their consistency, from the shape of the isotherms of the vapor-pressure lowering as a function of concn., and from approx. calcs. of the thickness of the layer of solvent around the rubber mols., it may be concluded that the solvent is bound by the mols. of jelly in the form of a solvated layer. The existence of such a layer within the sphere of action of the mols. explains a decrease in the activity of solvents, which results in a lowering of the vapor pressure, swelling pressure, etc., and makes the phenomenon similar to that of soln. C. C. DAVIS

Factors in the works control of plasticity by the Williams method. T. L. GARNER. *India Rubber J.* 78, 20(1929).—The influences of various dusting powders on plasticity detd. by the Williams method (cf. *C. A.* 18, 1763) were studied. The great differences are shown by the following results, which give the no. of sec. for the hand to cover 50 divisions on the gage: none 154, French chalk 85, Zn stearate 86, ZnO 146, colloidal ZnO 166, light MgO 157, heavy MgO 179, Mg carbonate 117, kieselguhr 83, S 151, lithopone 142, china clay 112, PbO 126, lime 47, red oxide 154, Ti white 117, C black 180, barytes 140, vegetable black 96, graphite 19, "Thermatomic" black 142, "Micronex" black 182, diphenylguanidine 18, triphenylguanidine 118, di-*o*-tolylguanidine 34, tetramethylthiuram disulfide 36, stearic acid 136. There was no relation between particle size and the effect on plasticity; other conclusions may be drawn by examn. of the data. The better the lubricating power of a substance between steel and rubber the lower the plasticity no., so that the expts. represent a method for detg. the lubricating effect of a powder. The fact that a powder may give a higher value than for clean rubber shows that some slipping occurs with clean rubber, and a mathematical interpretation of the plasticity values is impossible. C. C. DAVIS

Stripping tests and ply-adhesion of rubber-fabric belting. H. BRANDT. *Kautschuk* 5, 228; *India Rubber J.* 78, 845-6(1929).—In the stripping test, the stress required to sep. a partly stripped ply at a given rate was detd. In the ply-adhesion test, plies were left adhering over a definite square area (4 sq. cm.) and the pull was applied perpendicularly. Belts were made in 5 ways: (1) calender-frictioning; (2) spreader-coating; (3) multiple spreader-coating; (4) calender-frictioning plus spreader-coating and (5) spreader-coating plus calender-frictioning. Belts by method (5) gave the highest stripping tests, followed by methods (4), (3), (2) and poorest by (1). The av. values were 9.03, 6.38, 5.66, 3.36 and 2.08 kg., resp., per 2 cm. width. The press-pressure influenced the stripping of belts by (1), but not of belts by the other methods. In the ply-adhesion test, the same order of excellence was found but with much less range, *vis.*, 26.9, 20.9, 20.25, 17.38 and 17.3 kg. per 4 sq. cm. for belts of (5), (4), (3), (2) and (1), resp. The stripping test does not indicate the strength of adhesion so exactly as the ply-adhesion method. C. C. DAVIS

Comments on an article entitled "Stripping tests and ply-adhesion of rubber fabric belting" by H. Brandt. ERICH WURM. *Kautschuk* 5, 283-4(1929).—See preceding abstr. C. C. DAVIS

Temperature increases in rubberized fabric belting. H. BRANDT. *Kautschuk* 5, 250-5(1929). C. C. DAVIS

Rate of cure of reclaimed rubber. II. F. L. KILBOURN, JR., AND G. W. MILLER. *Ind. Eng. Chem.* 22, 69-73(1930); cf. Shepard, Palmer and Miller, *C. A.* 22, 1058.—The expts. supplement those previously described, which had shown that the alkali content of reclaimed rubber is only, in part, responsible for its rapid rate of vulcanization. Extn. of reclaimed rubber (made with alkali) with water for 60 days yielded 3 times as much alkali as that from an extn. of 4 hrs. Addn. of this quantity of alkali (in glycerol as a carrier) to reclaimed rubber made in water increased the rate of vulcanization to that of the reclaimed rubber made in aq. alkali. The new data confirm the lack of influence of combined S on the rate of vulcanization of reclaimed rubber. Further data indicate that residual accelerator (di-*o*-tolylguanidine) and oxidation products in reclaimed rubber do not affect the rate of vulcanization. On the other hand, residual alkali is largely responsible for the rapid rate of vulcanization of reclaimed rubbers. In addn. to its value as an accelerator, NaOH tends to improve phys. properties and resistance to Geer oven aging. C. C. DAVIS

The aging of [rubber] mixtures with reclaimed rubber and scrap rubber. WALTER HUTCHINSON. *Déchets et régénérés* 1929, No. 6, 2-3.—Representative formulas of hose are given to show mixts. with good aging properties. C. C. DAVIS

Recovery of volatile solvents. A. BOECLER. *Kautschuk* 5, 284(1929).—Comments on article by Piatti (cf. *C. A.* 24, 669). Reply. L. PIATTI. *Ibid* 284. [Further comments.] FIRMA MARTINE AND HÜNEKE. *Ibid* 284. [Closing remarks.] A. BOECLER. *Ibid* 6, 15(1930). C. C. DAVIS

The recovery of volatile solvents in India-rubber works. S. REGINALD PRICE. *Rubber Age* (London) 10, 492-4(1930).—An illustrated description, with particular reference to the "Acticarbone" process. C. C. DAVIS

The manufacture of starch for the rubber industry. GEOFFREY E. GOVIER. *Rubber Age* (London) 10, 490(1930).—A general description. C. C. DAVIS

Toxic substances in the rubber industry. VI. Lead and its compounds. P. A. DAVIS. *Rubber Age* (N. Y.) 26, 317-9(1929); cf. *C. A.* 24, 524.—The subject is treated in such a way that it is of interest also to the glass, porcelain, tile, paint, cable, dye, sizing and storage-battery industries. VII. Zinc and its compounds. *Ibid* 431-2(1930). C. C. DAVIS

Organic accelerators. I. FRED GROVE-PALMER. *Rubber Age* (London) 10, 485-6(1930).—A general description of their characteristics. C. C. DAVIS

Vulcanization accelerators and their use. II. FRIEDRICH EMDEN. *Kautschuk* 5, 269-76(1929); cf. *C. A.* 24, 750.—Seventy-three com. accelerators of various types are described. C. C. DAVIS

Determination of fiber and mechanical impurities in unvulcanized rubber. J. R. SCOTT. *India Rubber J.* 79, 158(1930).—The method is a modified form of the method of Spence and Kratz (*C. A.* 8, 3375), but an oxidizing agent is used to destroy the rubber. Swell the thinly sliced sample in CS₂ for 2 hrs., transfer the product to a 2% soln. of benzoyl peroxide in C₆H₆ (same wt. of peroxide as of sample), maintain at 34° until dissolved, filter through a Gooch filter, wash the residue with hot C₆H₆, ext. in a Schidrowitz app. for 3 hrs. with CS₂, then for 1 hr. with acetone, dry in an oven and weigh dry or after normal regain. Microscopic examn. will then tell whether the product is cotton, a mixt. of wool and cotton, etc. C. C. DAVIS

Thermodynamics of stressed vulcanized rubber. ROSCOE H. GERKE. *Ind. Eng. Chem.* 22, 73-7(1930).—The paper describes a method of obtaining equil. stress-strain curves of vulcanized rubber without appreciable hysteresis, and develops the thermodynamics of rubber under stress, utilizing for a beginning the 1st and 2nd laws of thermodynamics. The results show that the modulus of elasticity, when obtained from the equil. stress-strain curve, agree with calcns. by the 2nd law of thermodynamics and by the Joule heat effect. The modulus of elasticity calcd. from the equil. stress-strain curve is practically independent of the time of vulcanization for elongations not over 600%. On the other hand, the customary stress-strain curves show the stiffness to increase with increase in the time of vulcanization. These facts furnish additional evidence that the important effect of vulcanization is not to modify the elastic properties but to increase the resistance to plastic flow and permanent set. C. C. DAVIS

Advances in rubber for the automotive industry. WALTER C. KEYS. *Proc. Am. Soc. Testing Materials*, March 19, 1930, 15 pp.(preprint). E. H.

The application of electricity to the rubber industry. FREDERICK WALKER. *Trans. Inst. Rubber Industry* 5, 247-62(1930).—Illustrated, with data. C. C. DAVIS

Electrical preparation of raw rubber. M. BLASCHKE. *Chem.-Tech. Rundschau* 45, 67(1930).—A review. E. PICKERING

Studies of conditions affecting the vulcanization of rubber. III. Some properties of rubber with solvents. YUTAKA TOYABE AND KENJI FUKUNAGA. *J. Soc. Chem. Ind.*

Japan 33, Suppl. binding 7-9(1930).—Various substances were added to rubber solvents and the effects of these addns. on the soly. of raw rubber in these solvents were detd. by the obscurometry method described in a previous paper. The addn. of a small quantity of EtOH, AcMe or PhNO₂ increased the solvent power of C₆H₆ and of gasoline and similar effects were obtained by the addn. of inorg. bases and of org. accelerators. These phenomena are explained by Whitby's electro-viscous effect (cf. *C. A.* 19, 3035). During peptization of raw rubber in gasoline-EtOH or in gasoline contg. an org. accelerator, the gel-skeleton is easily dispersed, whereas dispersion proceeds with difficulty in gasoline alone. In the former case, many sub-microns were visible ultra-microscopically. The action of these accessory substances is similar to that of mastication as explained by Klein (cf. *C. A.* 19, 1064), i. e., a breaking down of the gel-skeleton and an increase in the no. of sub-microns. In the peptization of rubber in C₆H₆-EtOH dehydrated with calcined CuSO₄, the peptization max. coincided with the max. of mol. polarization of the mixed solvents given by Debye-Ostwald (cf. *C. A.* 22, 4031), at 33-5 mol.-% of EtOH. In all the expts. a mixt. of raw rubber and 20 vol. of ZnO was used. The results are given graphically.

The problem of vulcanization without sulfur, according to Ostromuiskii. WERNER ESCH. *Kautschuk* 6, 12-4(1930).—Various comments on the work of Ostromuiskii (cf. *C. A.* 24, 750).

The problem of vulcanization without sulfur. F. KIRCHHOFF. *Kautschuk* 6, 6-12 (1930).—An elaborated version of *C. A.* 24, 750, with photographic reproductions of vulcanizates without S.

The coloring of rubber. F. JACOBS. *Rev. gén. caoutchouc* 7, No. 58, 9-16(1930).—A general description of the properties and uses of inorg. coloring agents, with special discussions about ZnO, lithopone, Ti pigments, Mg carbonate, kaolin, pptd. BaSO₄, barytes, basic Pb sulfate, CaCO₃ and talc.

The specific gravity and the thermal expansion of the rubber-sulfur system. SUKEJI KIMURA and NOBORU NAMIKAWA. *J. Soc. Chem. Ind., Japan* 32, Suppl. binding 196-7 (1929).—There is usually a kink in the thermal expansion curve of rubber-S mixts. which occurs in the temp. range where the rubber changes from soft to hard, viz., at approx. -85°. An increase in S shifts the kink to higher temps., but toward 32% S the shifting gradually disappears. Above the temp. of the kink, the coeff. of thermal expansion is large; below that temp. it is small. As a result, the S-thermal expansion coeff. curve shows a sudden change at a definite range of S and at a definite temp. With increase of temp., this descending part is shifted toward the higher % S, and the general trend of the curve is modified. At a given temp. the S-d. curve also has a kink at a definite S content which is shifted toward the higher % S with increase of temp. The expts. show kinks in the S-d. curves at 14, 17, 20, 24 and 28% S, corresponding to 4°, 20°, 40°, 60° and 80°, resp. The temps. at which the kinks appear in the thermal-expansion curves are not sharply defined. If the kink in the S-d. curve bears some relation to the definite compd. mentioned by Curtis (cf. *C. A.* 22, 330), then there are an infinite no. of compds. which correspond to an infinite no. of kinks shifting to the higher S with increase of temp. This is improbable.

What is the reason for the use of hard rubber dust in hard rubber mixings and what advantages has it? FRANK BATH. *Rev. gén. caoutchouc* 7, No. 58, 5-6(1930).—A discussion. The chief advantages are the properties imparted during mixing and milling of new mixts., less contraction during molding, and easier control of the vulcanization process.

Drying of reclaimed rubber and of raw rubber in sheets. B. LAGRANGE. *Caoutchouc & gutta-percha* 27, 14,885-7(1930).—An illustrated description, with special reference to the relative economy of different systems.

Recovering lead in rubber factory. F. L. HAUSHALTER. *Chem. Met. Eng.* 37, 92 (1930).—Comparative tests of the tensile strength of Pb at various stages of the Pb process of molding in the manuf. of hose or wire showed that the tensile strength is increased and the elongation is decreased by the extrusion process. However, the Pb reverts to its original properties on cooling after the vulcanization process. The tensile strength-temp. curve (up to 280°F.) is an approx. straight line. At 280°F. the Pb began to yield at a stress of about 600 lb. per sq. in. The following data give tensile strengths at 80° and 280°F., resp.: pure pig 1880, 1239; tube before vulcanization 1930, 1345; tube after vulcanization 2390, 1385; refined dross 1810, 1180; dross 400, 650. A table of wall thicknesses for various hose diam. can be tabulated with the aid of an assumed safe working stress and the formula $PD = 2tf$, where P is the effective pressure, D the inside diam., t the thickness of wall and f the working stress.

Spray-drying latex in Sumatra. HENDRICK DE LEEUW. *Chem. Met. Eng.* 37,

100-2(1930).—An illustrated description of the Hopkinson process and of the properties of the rubber obtained. C. C. DAVIS

Rubberizing of fabrics for belting by means of concentrated latex. P. W. HUTCHINSON. *Rev. gén. caoutchouc* 7, No. 58, 7(1930).—A discussion, with representative formulas, of the results obtainable in the manuf. of belting by impregnation of the fabric with compounded latex. With 450 g. of dry mixt. per sq. m. of fabric, a "friction test" of 15-19 kg. per 2 cm. width can be obtained. Vulcanization with ultra-accelerators can be carried out by a continuous process, with very short times of cure. C. C. D.

Technology of latex. A survey of the patent literature of recent years. ALADIN. *Gummi-Ztg.* 44, 685-8(1929); 44, 737-8, 787-8, 837-8, 894-6, 945-6(1930); cf. C. A. 23, 2320.—Two hundred twelve patents are described. C. C. DAVIS

Thermodynamics of rubber. I. Rubber as a system of two phases. L. S. ORNSTEIN, J. G. EYMERS and Miss J. Wouda. *Proc. Acad. Sci. Amsterdam* 32, 1235-42(1929).—Measurements of v. Geel and Eymers (cf. C. A. 23, 4099, 5611) of the elongation of raw rubber as a function of stress were repeated, with addnl. measurements of the changes of width and thickness as a function of the stress. The rubber was prepd. as before. The % diminution in width and in thickness showed the same functional relation to the stress as did the length. By differentiation of the stress-strain curve, a curve representing the modulus of elasticity as a function of stress was obtained. From the relation between the stress and change in dimensions, with differentiation of the stress-contraction ratio curve, a curve showing the modulus of contraction as a function of the stress was constructed. Thirdly, with data from the earlier work, curves were constructed showing the relation between stress and double refraction as a function of temp. Lastly, the influence of temp. on the stress-strain curve was detd. All results indicate that at a stress of about 6 kg. per sq. cm., there is a change in the structure of rubber. This transition point is, however, displaced to lower stress values and higher elongations with increase in temp. Numerous detns. around the transition point with a special *app.* with an automatic registering contrivance showed a sudden change in the function, *i. e.*, a transition at approx. 70% elongation, as in the previous expts. This change from 1 phase to another was sudden, and the gradual change observed by Katz is explained by the long duration and the temp. fluctuations of his measurements. By utilizing the Clapeyron equation for phase changes, which for rubber is: $dK/dT = -r/[(l_2 - l_1)T]$, where K is the force, r the latent heat and $l_2 - l_1$ the increase in length per unit length, measurements showed that at the transition point K is proportional to $\log T$, which suggests a phase change. Calcs. (with $l_2 - l_1$ 5%) of the heat of transition gave 4×10^{-3} cal. per unit vol. Expts. are in progress in which the heat of transition is detd. by expt. Data on the influence of temp. on the elongation as a function of stress show that the linear coeff. of expansion of raw rubber is pos., which is also confirmed by the linear coeff. of unstretched rubber. According to the 2nd law of thermodynamics, this is contrary to the rise of temp. of rubber when stretched. Therefore, this pos. coeff. of elongation causes cooling during elongation and the heating effect can be explained only by hysteresis, which expts. showed to be considerable. The heat of hysteresis thus overbalances the cooling effect. Expts. showed a neg. coeff. of expansion of vulcanized rubber and an inappreciable hysteresis. The thermodynamics of this will be reported in a forthcoming paper. A study of the stress-strain curve of vulcanized rubber indicated that here there is no transition of phases up to the breaking point. C. C. DAVIS

Compounding ingredients for rubber. WEBSTER NORRIS. *Kunststoffe* 18, 226-8(1928); *India Rubber World* 78, No. 3, 57-9(1928).—The principles of coloring, the characteristics of org. colors for rubber products and the general difficulties of vulcanization with org. colors are discussed. B. HAMILTON

Some properties of carbon black. D. PARKINSON. *Trans. Inst. Rubber Industry* 5, 263-83(1930).—A crit. discussion of different types of C blacks of interest in rubber manuf., with new data. Carbon blacks are defined as all varieties of moderately pure C having the form of soot. They include therefore gas black, acetylene black, lampblack and thermatomic black. The subjects include particle size, shape and structure, the relation of these properties to the behavior of blacks in rubber, the degree of blackness, adsorptive capacity, volatile components (adsorbed gases) and dispersion in general. None of the methods of various investigators for detg. particle size gives any information about the distribution of sizes. Expts. by P. on gas black confirm the observation of Grenquist (cf. C. A. 23, 4097) that $200\mu\mu$ is the upper limit. Considerable material with particles of diam. under $50\mu\mu$ was found. With lampblack, distribution curves of P. support the observations of Green (C. A. 17, 1338) with an optimum at 0.3-0.6 μ and a fair proportion of particles at 0.5-1.0 μ . Preliminary tests on acetylene black indicate that its particles are intermediate between gas and lampblack. Contrary to Blake (cf. C. A. 22, 4876) reinforcing power is not independent of particle

size, for it does not depend simply upon the interfacial energy between rubber and filler. The smaller the particles the greater is their intrinsic free energy (because of the higher degree of curvature); so the smaller the particle the greater is the free surface energy, *i. e.*, the greater the energy per unit surface area. The term *energy absorption* (cf. Dawson, *C. A.* 23, 5351) is preferable to resilient energy capacity or proof resilience (cf. Wiegand, *C. A.* 19, 3386) for the idea of energy input. Curves (from Healey) show the effects of the addn. of increasing vols. of gas black, lampblack and acetylene black on resilience and hardness. Resilience was detd. by the rebound of a pendulum from a rigid rubber block, and the hardness by calcn. from the velocity of impact and degree of distortion. At all concns. gas black gave the lowest resilience, and lampblack the highest. ZnO and Mg carbonate up to high concns. increased the resilience, so the behavior of the blacks cannot be explained merely by an increasing friction during deformation between rubber and filler. There was little distinction among the blacks in their effects on the hardness, and there was little or no relation between hardness and particle size. There is no evidence for the hypothesis of Spear (cf. *India Rubber World* 71, 18(1924)) that the surface of black particles is serrated. Preliminary expts. on the adsorption of gases indicate that the degree of adsorption of C blacks is a function of the sp. surface, *i. e.*, the smaller the particle size the more the gas adsorbed. This supports the work of Goodwin and Park (cf. *C. A.* 22, 3802), and of Carson and Sebrell (cf. *C. A.* 23, 5351). The monomol. layer theory originating with Langmuir (*C. A.* 9, 1562) and applied by Johnson (*C. A.* 22, 4273) to the presence of O on blacks is not contradicted by any data on gas blacks, but it does not hold true of lampblacks. There is some relation between dispersion and ease of wetting of a filler by rubber, and this wetting phenomenon involves the surface angle of contact. Where wetting is perfect this angle is approx. 0, and the diminution in surface tension is a max. With very small particle size, the angle of contact is probably close to 0, but it is not known whether it varies with fillers of the same size and shape of particle. There is no proof that the reinforcing effect of chemically inert ingredients depends upon factors other than those which can be attributed to particle size, shape and degree and extent of dispersion. According to Blake (*C. A.* 22, 4876; 23, 4595) fatty acids, natural or added, are the dispersing agents of C black and not the rubber, and the acids normally present in rubber are just enough to form a monomol. film with 30 vols. of black per 100 vols. of rubber. However, 0.2μ is much too high a value for the diam., and actually 3-4 times the surface is present. Accordingly 3-4 times as much fatty acid as calcd. by Blake is necessary. Moreover, according to the theory, it would be difficult or impossible to disperse gas black in rubber contg. no fatty acids. Two mixts. of rubber and gas black (100:50) were prepd., one with normal rubber, the other with acetone-extd. rubber. The black mixed easily into the latter and microscopic examn. showed that it was as well dispersed as in the unextd. rubber. In dil. xylene, each mixt. gave the amber tint of good dispersion. Attempts to disperse gas black in stearic acid solns. were unsuccessful, so stearic acid has little or no influence on the dispersion of black in rubber (cf. Depew, *Rubber Age* 24, 378(1929); Goodwin and Park, *loc. cit.*). **Discussion.** LAMBOURN. *Ibid* 280.—Rubber mixts. the same except for different types of C blacks have widely different heat conductivities. The lowest values were obtained with gas black, then lampblack and the highest with acetylene black. MADGE. *Ibid* 280.—Dispersion of 5-10% of black in a thin aq. medium in a colloid mill gives a stiff paste. This may be related to the stiffening of rubber by blacks. C. C. DAVIS

The solvation of high molecular substances, with special reference to that of rubber. PAUL STAMBERGER and CLAUDE M. BLOW. *Kautschuk* 6, 22-7(1930).—A review of the literature on solvation phenomena leads to the conclusion that actual combination takes place between the solvent and the micelles of high mol. substance. This is true of rubber (cf. S., *C. A.* 24, 1762). There is no linear relation between depression of vapor pressure and concn., and the depressions are measurable only below a definite concn. At the smallest depressions the solvent layer is approx. 1.5-2.0 A. U., which agrees with the theory of Staudinger (cf. *C. A.* 24, 1563). The tendency of rubber to swell was the same regardless of the origin of the rubber, and agreed well with the data of Posnjak (cf. *Kolloidchem. Beihefte* 3, 417(1921)), supporting the idea that rubber is a single definite compd. (cf. Pummerer, Nielsen and Gündel (*C. A.* 22, 886)). The *app.* used in these expts. is described and illustrated. The expts. were at 25°, with PhMe as solvent. The swelling pressures (solvation pressure) as a function of concn. were measured. The results indicate that combination of rubber and solvent is a mol. process, but that it takes place in a manner quite different from that with smaller mols. No portion of the curve was in accord with the van't Hoff equation, so the solvent is held to rubber by forces far different from those in solns. of the same concns. where the osmotic pressure is proportional to the concn. The osmotic pressure showed no

linear relation to the concn., and the data indicate that rubber does not go into soln. in the way that substances of low mol. wt. do. The solvation pressures of dead-milled rubber are no different from those of unmilled rubber and the differences in swelling pressures of milled and unmilled rubber previously reported by S. (cf. *C. A.* 23, 4846) arose from errors in technic, because of extremely slow diffusion. The new data give no indication of depolymerization. Any connection between viscosity of a soln. and the mol. wt. of the solute has no theoretical basis, and the present data indicate the error of this viewpoint. The viscosities of mixts. of dead-milled rubber and gas black showed no relation to the mol. wt. as suggested by Staudinger and by Mark and Fikentscher. The viscosity of highly masticated rubber solns. increased with the proportion of gas black milled into the rubber, and this increase was relatively greater with concd. solns. When the solns. were prepd. some time after milling, the viscosity was higher. Mixts. which shortly after milling had the plasticity of overmasticated rubber became firm and elastic after aging. This change was followed by the changes in the viscosities of the corresponding solns. These solns. were highly thixotropic; this agrees with the explanation of McBain for the reënforcing action of fillers (cf. *C. A.* 21, 3510) and with that of Klein and S. for mastication (cf. *C. A.* 19, 1064). Changes in the viscosity of solns. of rubber treated in different ways are not the result of depolymerization, but of a change in structure or orientation of the rubber particles. Accordingly viscosity detns. are of no service for detg. mol. wts. of such substances. The expts. give no clue to the manner of dispersion of rubber in soln. and measurements of monomol. layers tell no more, but only that the forces of attraction of the free liquid surface upon certain polar groups of the mols. are greater than the forces of attraction. In any case the dispersion of such substances in soln. is highly complicated. C. C. D.

Accelerators of vulcanization and their uses. FRIEDERICH EMDEN. *Rubber Age* (N. Y.) 26, 659-61 (1930).—See *C. A.* 24, 1763. C. C. DAVIS

Cultivation and preparation of rubber in the United States. D. SPENCE. *Ind. Eng. Chem.* 22, 384-7 (1930).—An illustrated description of recent botanical, chem., agricultural, mech. and economic development in the cultivation and extn. of rubber from Mexican guayule in California (cf. *C. A.* 20, 3841). C. C. DAVIS

Factory economics in the preparation of raw rubber. B. J. EATON. *Rubber Res. Inst. Malaya, Quart. J.* 1, 232-40 (1929).—Mech. equipment is described. C. C. DAVIS

The chemistry of rubber. HARRY L. FISHER. *Chem. Reviews* 7, 51-138 (1930).—A general review of recent progress, dealing with (1) latex and raw rubber, including production, sources of raw rubber, the origin, function, properties, concn. and uses of latex, and the character of vulcanization; (2) the rubber hydrocarbon, including its isolation and properties, cryst. rubber, mol. wt. and other phys. properties, action of heat and its structure, and (3) chem. reactions of rubber and its derivs., including halogen products and their derivs., hydrohalides and their derivs., the action of S, S₂Cl₂, Se, SeOCl₂, O, O₃, oxidizing agents, H, C(NO₂)₄, HNO₃, CrOCl, SnCl₄, FeCl₃ and H₂SO₄, "nitrosites," nitrones, polycyclo-rubbers, characteristics and theories of vulcanization, acceleration and aging. Two hundred forty-six references are appended. C. C. D.

The common factors of technical and works control in the rubber and chemical industry. H. C. YOUNG. *J. Soc. Chem. Ind.* 49, 165-8T (1930).—A general discussion dealing with the distinction between technical and works control, the desiderata of technical and engineering staffs, control of raw materials, storage, process control, final test control, service control, waste, labor costs, quantity control and quality of products and labor. C. C. DAVIS

Handling equipment effects economies in a rubber factory. JAMES A. LEE. *Chem. Met. Eng.* 37, 229-31 (1930). E. H.

The coloring of rubber. F. JACOBS. *Rev. gén. caoutchouc* 7, No. 59, 9-18 (1930); cf. *C. A.* 24, 2327.—The characteristics of various inorg. and org. colors are described. C. C. DAVIS

The use of reclaimed rubber and old rubber without any raw rubber with the aid of Sipalin. RUDOLF DITMAR AND KARL H. PREUSSE. *Déchets et régénérés* 2, No. 7, 2-3 (1930).—Added to new rubber and reclaimed rubber mixts., Sipalins render the mixts. tacky and capable of absorbing large proportions of fillers. They also improve the calendaring of such mixts. and make it possible to use ground scrap directly in mixts. With the aid of Sipalins, hard rubber can be made with reclaimed rubber and no new rubber. Typical formulas contg. Sipalin A. O. M. and M. O. M. are given (cf. *C. A.* 24, 1247). C. C. DAVIS

Organic accelerators. III. FRED GROVE-PALMER. *Rubber Age* (London) 11, 54-5 (1930); cf. *C. A.* 24, 1763.—The characteristics of very active accelerators are described. C. C. DAVIS

Ultra-accelerators. G. DUMONTIER. *Rev. gén. caoutchouc* 7, No. 59, 7-8(1930).—A general discussion dealing in particular with monosulfide and disulfide of tetramethylthiuram. C. C. DAVIS

Mode of action of organic accelerators of vulcanization. PAUL BARY. *Rev. gén. caoutchouc* 7, No. 59, 3-6(1930); cf. C. A. 23, 5612.—A review and discussion. C. C. DAVIS

The manufacture of sponges. P. W. HUTCHINSON. *Rev. gén. caoutchouc* 7, No. 59, 23-5(1930).—A description, with diagrams of app. C. C. DAVIS

The difference between ultramarine and Thénard blue in rubber mixtures. RUDOLF DITMAR AND KARL H. PREUSSE. *Gummi-Ztg.* 44, 1355-6(1930); cf. C. A. 23, 5351.—Comparative tests of the behavior of ultramarine blue (I) and of Thénard blue (II) in various rubber mixts. show that (1) II does not lose its color in S_2Cl_2 vulcanization, whereas I is bleached; (2) the colors obtained with I are deeper and more attractive than the lighter "dove" blues obtained with II; (3) II is stable during vulcanization with most accelerators, whereas I fades with many accelerators and (4) II is more expensive to use than is I. C. C. DAVIS

The numerical calculation of the deformation curves of rubber. M. KRÖGER AND E. MÖBIUS. *Gummi-Ztg.* 44, 1153-4, 1209-12(1930).—The exptl. data deal with vulcanized rubber. Power series, Fourier series and exponential functions were all inapplicable as expressions of the deformation curves. Curves obtained by a single and by double stretching were then studied. In the 2nd case a hyperbolic tangent was an approx. representation, and in the 1st case the integral of the error in combination with its 1st deriv. of the 4th power. However, both failed at very low elongations, and further consts. had to be added. This applied also to the functions of Einstein and Debye which represent the relation between sp. heat and temp. and which were applied to the present data. On the other hand, by adding a factor of 5 consts. to the Einstein function and by introducing a quadratic transcendent and using a new function with 3 or 4 consts. in the Debye law, changes were made in these expressions which made them conform to the deformation throughout. This last method of representation is accordingly the best. The theoretical aspects were only touched upon, but will be treated more fully later. No calcns. were made to show whether these new functions are applicable to other cases of elastic deformation and to problems of magnetization. C. C. DAVIS

The testing of automotive rubber parts assembled under compression. I. Deflection and compression. II. Compression-set and some special tests. FRANZ D. ABBOTT. *Ind. Eng. Chem., Anal. Ed.* 2, 145-59(1930).—The investigation is an attempt to establish uniform methods for detg. the behavior of rubber parts when compressed. High tensile strength is not a criterion of the permanent set after compression, nor is hardness a measure of deflectability. Moreover, deflection and permanent set under compression are greatly influenced by the size and shape of the test piece, the method of cutting the sample, the thickness and the character of the contact surface. Compression and compression-set app. are discussed, and a newly designed lab. app. is described. A *compressetometer* is very useful for detg. deflection, hysteresis and set, and these detns. may be performed under const. load or const. distortion. A const. load compression-set clamp is suggested as a lab. standard for permanent-set detns. A discussion of the chief factors in the formulation of a compression-set test leads to the conclusion that a const. load test is preferable to a const. deflection test. Special cases, such as the flexometer test and impact test for bumpers, are also discussed. C. C. DAVIS

Hard rubber dust. Some of its applications, and a comparison between hard rubber and synthetic molding powders. FRANK BATH. *Rev. gén. caoutchouc* 7, No. 59, 20-2(1930).—A general discussion. C. C. DAVIS

The applications and analysis of latex. W. H. STEVENS. *Trans. Inst. Rubber Industry* 5, 362-74(1930).—A general review and discussion. C. C. DAVIS

Natural and synthetic rubber. IV. 4-Methyl-4-octene by isoprene ethylation. THOMAS MIDGLEY, JR., AND ALBERT L. HENNE. *J. Am. Chem. Soc.* 52, 2075-7(1930); cf. C. A. 23, 2848.— $H_2C:CMcCH:CH_2$ and $EtBr$ with K in Et_2O give 4% of 4-methyl-4-octene, b. 139° , d_{20}^{20} 0.7495, n_D^{20} 1.4228; no trace of any other compd. was detected. The structure of this none, which was established by the action of O_3 , is in agreement with the usual behavior of a conjugated double bond system. This type of addn. is further evidence in favor of the hypothesis which regards the polymerization of isoprene to synthetic rubber as the formation of long chains of isoprene units linked together by ordinary valences in the 1,4-position. V. Tetramethyloctadiene. *Ibid* 2077-8.—Dimethylbutadiene, $EtOH$ and K at 70° give 2,3,6,7-tetramethyl-2,6-octadiene and methylrubber. The diene b. $87.5-85.5^\circ$, d_4^{25} 0.7971, n_D^{25} 1.45963. Hydrogenation

gives 2,3,6,7-tetramethyloctane, b_{20-22} 92°, d_4^{25} 0.7593, n_D^{25} 1.42527. If the condensation is carried out at a low temp., a mixt. of compds. is obtained. The structure of the diene is used as an evidence that the methylrubber formula must be a long, open chain. This is also regarded as an evidence in favor of the chain formula of natural rubber.

C. J. WEST

Isoprene and rubber. XVI. Constitution of rubber. H. STAUDINGER AND H. F. BONDY. *Ber.* 62B, 2411-6(1929); cf. *C. A.* 23, 4097.—By the degradation of rubber or gutta-percha by heat or by Zn and HCl there can be obtained cyclo products with the properties of hemi-colloids; as these properties differ entirely from those of rubber and gutta-percha themselves (*e. g.*, the viscosity of the solns. of the degradation products is very much lower) it was concluded that rubber and gutta-percha have much higher mol. wts. than their degradation products. This conclusion is valid, however, only if the structure of the degradation products can be established, and it can be proved that they are not assocn. products. Attempts to prove this by hydrogenation (*cf.* *C. A.* 24, 3002) met with difficulties, as will be reported later. The desired proof was, however, obtained in an entirely different way. Cyclorubber and cyclogutta-percha are unsatd. and on standing in the air autoxidize. Various preps. which had stood in air over P_2O_5 for 2 yrs. were found to have absorbed an atom of O to every 3-8 isoprene groups, but their av. mol. wt., the viscosity of their solns. and their liquefying temp. had not materially changed. This is considered proof that the values obtained in mol. wt. detns. on these cyclorubbers are correct and not the result of assocn. phenomena, and that the differences in the viscosities of solns. of various preps. are really due to differences in mol. magnitude. Meyer and Mark have recently expressed the opinion that rubber consists of micelles made up of bundles of chains contg. 75-150 isoprene residues. Now, the above cyclo products with av. mol. wts. of 5000-10,000, contain equally long chains and yet form no micelles in soln. Rubber consists of far larger mols. and its characteristic properties are due to the size of these mols., not to any special micellar character.

C. A. R.

Isoprene and rubber. XVII. The fractionation of balata. H. STAUDINGER AND H. F. BONDY. *Ber.* 63B, 724-30(1930); cf. preceding abstr.—Previous expts. by S. and his collaborators have shown that synthetic compds. of high mol. wt. consist of mixts. of homologous polymers, and it was therefore assumed that natural products of high mol. wt. are likewise mixts. of the same character. This is already well established for rubber and gutta-percha, so expts. were directed toward balata. Balata latex was dild. with water and pptd. with MeOH, with the same subsequent procedure as with gutta-percha (*cf.* *C. A.* 23, 3372). Sepn. of the balata into fractions was easy because it crystallizes from warm C_6H_6 , PhMe or xylene on cooling, and by using different temps. various fractions are obtained. It was assumed that the higher the mol. wt., the less the soly. and the earlier the sepn. To show the presence of substances of different av. mol. wts. in the resp. fractions, viscosities of solns. of the fractions were detd. It had already been proved that with semi-colloids, differences in viscosity are due to differences in mol. wt. (*cf.* S., *C. A.* 21, 1271; S. and Heuer, *C. A.* 24, 2993; S. and B., *C. A.* 23, 3372), and similarly it was found that balata (a homopolar hydrocarbon) is molecularly dispersed in dil. solns. and forms no micelles. The viscosities of the fractions diminished with increase in soly., so balata consists of a mixt. of polymeric homologs, which differ in their length of mol., though this is true only if the fractions are polymerically uniform. It was possible that the more sol. portions had different structures from those of the less sol. portions. Balata might consist of cyclized compds., so detns. were made of its double bonds before fractionation, and then after fractionation the double bonds of the initial and last fractions were detd. There was one double bond to each base mol. in all cases, so the balata fractions were polymerically uniform. With xylene solns. of purified balata there were obtained fractions of 6, 5, 2, 0.8 and 3 g. at 10°, 5°, 3°, 0° and -12°, resp. The expts. in general show that balata is a mixt. of compds. of high and low mol. wt. All expts. were carried out in the absence of O, but even then there was the possibility that balata is so sensitive that it had already oxidized and its structure changed, and it was not proved that balata, like highly polymerized synthetic substances, consists of polymeric homologs. As with polystyrols, deviations from the law of Hagen-Poiseuille were greatest in solns. with the highest viscosities, *i. e.*, with the largest mols. Hence the deviations are not caused by any structural characteristic of the soln. but by the presence of large mols. (*cf.* S. and Frey, *C. A.* 24, 1564; Ostwald, *C. A.* 19, 2288).

XVIII. Studies of the viscosity of balata. H. STAUDINGER AND E. O. LEUPOLD. *Ibid* 730-3.—A review of recent literature shows the diverse views prevailing with regard to the mol. state of rubber in colloidal soln. If the colloidal particles are aggregated or are in micellar form, their size should diminish with increase of temp. and with de-

crease in the sp. viscosity of their soln. If, however, the solns. are mol., the sp. viscosity should be the same at different temps. (assuming no decompn.). This problem has already been studied with polystyrol (cf. S. and Heuer, *C. A.* 24, 1565), and in the present paper the work is extended to balata. Anomalous results were obtained except when all O was excluded; in fact, balata and rubber were found to be so sensitive to air that the viscosity of their solns. diminished from this cause alone, whereas in N there was no diminution even after prolonged heating at 60°. Polystyrols are much more sensitive to reagents and to heating than are substances made up of semi-colloidal mols., and the lability of the balata mol. is much increased (compared with polystyrol) because of the presence of the double bond. Therefore, balata is much more sensitive to O than polystyrol macromols. The min. proportion of O necessary to cause marked decompn. of balata is evidenced by the reaction: $[(C_6H_5)_{375}(C_5H_8)_{375}] + O_2 \rightarrow 2(C_6H_5)_{375}O$, where the oxidation product contains only 0.06% O. This reaction can be followed only by changes in viscosity. This suggests the increasing importance of viscosity detns. in studying compds. of high mol. wt., for the viscosity is a function of mol. wt. By excluding O, it was possible to ascertain whether balata mols. or micelles are present in dil. solns. Expts. show that mols. are present, for the sp. viscosity of 0.025, 0.05 and 0.1 molar solns. changed little or not at all on heating at 60°. Moreover, expts. showed that balata mols. are not strongly solvated as assumed by Fikentscher and Mark (cf. *C. A.* 24, 1010) with rubber, for a solvate film would vary with increasing temp. and this would be evidenced by a marked decrease in viscosity. It is of great importance whether colloidal particles in soln. are large mols. (macromols.) or micelles, *i. e.*, whether changes are caused by internal rearrangement or by variations in particle size as assumed by org. chemists. The present expts. prove definitely the existence of macromols. XIX. The molecular size of rubber and balata. H. STAUDINGER AND H. F. BONDY. *Ibid* 734-6.—On the basis that both rubber and balata solns. contain only macromols., it is possible to calc. the mol. wts. from viscosity detns. by the formula $M = \eta_{sp.}/(CK_m)$ (cf. S. and Heuer, *C. A.* 24, 2993), with the assumption that the mols. are in single and double thread form. K_m is detd. by heating rubber and gutta-percha in tetralin or xylene which gave semi-colloidal decompn. products, and the av. mol. wt. could be detd. It was 0.3×10^{-3} . Rubber and gutta-percha are supposed to be stereoisomeric (cf. S. and B., *C. A.* 23, 3372) and balata is supposed to be identical to gutta-percha, but the exptl. constns. of rubber and gutta-percha were the same, though with the *trans*- and *cis*-forms of dichloroethylene they are different (cf. Herz, *C. A.* 11, 2631). The viscosities of rubber and balata solns. were detd. at such low concns. that they were comparable to semi-colloid solns. Expts. show that under these conditions the viscosity increases with the concn., so the sp. viscosities of molar solns. could be calcd. and from these the mol. wts. The mol. wt. of balata before fractionation was 51,000, that of the Et₂O-sol. fraction of rubber purified by the method of Pummerer was 52,000 and that of the difficulty sol. fraction of rubber was 73,000. Similar values for rubber and gutta-percha were obtained by Caspari by osmosis (cf. *C. A.* 9, 170). From different points of view similar values have been obtained for the rubber micelle by Pummerer (*C. A.* 22, 886), Kröpelin and Brumshagen (*C. A.* 23, 4123), Meyer and Mark (*C. A.* 23, 1524) and Ostwald (*C. A.* 24, 2356). The viscosity measurements in the present paper confirm theories based on chem. studies of the size of macromols. (cf. S. and Fritsch, *C. A.* 17, 2974). If these mols. are composed of high mol. rings, comparable to double threads, their length would be approx. 2000 A. U. If they are simple long thread mols. their length is approx. 4000 A. U., in which case they would have in 1 dimension the wave length of visible light.

C. C. DAVIS

Rubber and its application to textiles. DONALD H. POWERS. *Am. Dyestuff Repr.* 19, 89-95(1930).—A review and discussion.

MILTON HARRIS

Rubber manufacture. S. S. PICKLES. *Chemist and Druggist* 111, 717; *Pharm. J.* 123, 562-3(1929).—A lecture on the history of rubber, its chief sources, manuf. and methods of preventing deterioration of rubber articles.

S. WALDBOTT

The interfacial energy between rubber and fillers. FRITZ HARTNER. *Kolloid-chem. Beihefte* 30, 83-108(1929).—The purpose of the investigation was to increase the precision and make more reliable the colorimetric method of Bostroem (cf. *C. A.* 22, 4271) and to discover and overcome any difficulties or sources of error in its application to rubber. The expts. deal with (1) the relation between the reënforsing action of a filler and its concn. and the utilization of the interfacial energy between rubber and filler; (2) the evaluation of the surface tension in the system: raw rubber/filler; (3) aging and the possibility of reversing it; and (4) a comparison of various com. gas blacks at the same concn. The colorimeter was similar to that of Bostroem (*loc. cit.*). The modified *app.* and the technic are described in detail and illustrated. Data on the

work of rupture, reinforcing action and heat of wetting lead to the conclusion that the higher the concn. of a filler, the lower the proportion of its available surface energy which is utilized, and at the higher concns. the filler acts more and more merely as ballast. Ideal mixts. where every particle is wet with rubber, with no agglomerates, is not approached in present-day practice. The extent to which a filler is utilized is expressed by U_c/U_o , and the following data give this ratio for gas black and ZnO, resp., at 8.5, 17, 25.5 and 34% by vol., resp.: 0.42, 0.32; 0.31, 0.32; 0.27, 0.20; 0.25, 0.17. Because ZnO is coarser than gas black, the capacity factor of its surface energy is smaller, which means that its intensity factor (interfacial energy between rubber and ZnO) must be greater. Expressing the heat of adhesion, not on unit vol. of filler, but on mixt., the interfacial energy is 0 at both 0 and at 100% concn. and the U curve starts from 0, passes through a max. and becomes 0 again at 100%. The ratio A/U , where A is the work done by the system and U is decrease in total energy, was approx. 0.5 in all cases. Detns. of the size of gas black particles (by T. Peterfi) gave an av. of 0.025 μ . The heat of swelling of rubber increases with aging, e. g., rubber, which when new showed 0.15 cal. per g., showed after 1 yr. over 4 cal. per g. When aged rubber was remilled, it gave the same heat of swelling as when new, so the mech. effect of mastication combined with the elevated temp. ruptured the bonds between rubber mols. resulting from aggregation, though swelling alone did not do so. Further expts. showed that, to an approx. degree, the reinforcing values of different gas blacks varied directly with their heats of swelling and therefore with their surface energy. C. C. DAVIS

A comparison of the effect of pigment reinforcement of crude and reclaimed rubber. J. STOFFORTH. *Trans. Inst. Rubber Industry* 5, 356-61(1930).—The exptl. results of Winkelman and Croakman (cf. C. A. 22, 1059) were reexamined in the light of a paper by Lunn (C. A. 23, 3371) and the reinforcement of reclaim mixts. contg. various concns. of pigment was ascertained. In the latter work the method was to add to the base mixt.: whole tire reclaim 100, S 5, different proportions of barytes, ZnO, "Thermatomic C" and gas black, resp., and to det. the elongation-total pigment energy curves and the elongation-pigment energy per unit vol. of pigment curves of the cured mixts. Increases of energy by pigments were much less with reclaimed rubber than with new rubber. Both in the new rubber and reclaim mixts., gas black had a pronounced reinforcing and stiffening effect. "Thermatomic C" also reinforced the reclaim mixt.; stiffening was proportional to the quantity added; the tensile strength increased with the content, and the ultimate elongation remained almost unaltered. The energy values were lower than those with gas black. ZnO had a reinforcing effect, with a slight progressive increase in stiffness with increase in ZnO, and, in general, its behavior was like that of "Thermatomic C." Barytes had the least reinforcing power, with progressive decrease in elongation and no increase in tensile strength. With gas black and with "Thermatomic C," the sp. reinforcing power increased progressively with elongation and with increase in proportion of pigment, and also with ZnO to a much smaller degree. With barytes the sp. reinforcing power was const. for the various proportions and at different elongations. In general, the relative behavior of the pigments was the same in reclaim mixts. as in the rubber mixts. of Lunn. C. C. DAVIS

The manufacture of reclaimed rubber. R. F. PEARSON. *Trans. Inst. Rubber Industry* 5, 336-40(1930).—A general description followed by a discussion. C. C. D.

The use of powdered scrap or of reclaimed rubber. PAUL BARY. *Déchets et Régénérés* 2, No. 8, 4-5(1930).—A discussion of the relative merits for various purposes. C. C. DAVIS

The testing of reclaimed rubber. W. E. STAFFORD. *Trans. Inst. Rubber Industry* 5, 340-8(1930).—A review and discussion of present-day developments and methods of control, including detns. of moisture, d., ash, MeAc ext., CHCl_3 ext., alc. KOH ext., alky., combined S, C, rubber, vulcanizing properties, aging and plasticity. A general discussion follows the paper. C. C. DAVIS

Reclaims from the rubber manufacturer's standpoint. E. H. HURLESTON. *Trans. Inst. Rubber Industry* 5, 348-55(1930).—A general discussion, with certain quant. data. Plasticity detns. of reclaimed rubbers (in which the samples were mixed with an equal wt. of new rubber and tested on a Griffiths plastometer (cf. C. A. 20, 2094), showed the following values: whole tire (alkali process) 8.0-9.0; solid tire (alkali process) 7.0-9.5; red tube (alkali process) 10.5-27.5; gray tube (alkali process) 3.0-4.5; mech. goods (alkali process) 7.0; red tube (oil heater process) 17.0; tire tread (oil heater process) 10.0; rubber (same milling) 18.0. The higher the values are the harder and more nerry the product is, so a reclaim of high quality may give a mixt. less plastic than new rubber. The softening action of whole tire reclaim agrees with the conclusions of Swishe and Sanders (*Rubber Age* (N. Y.) 10, 559(1925)), but the reverse effect of alkali tube reclaim is unexpected. Tests show that different results are obtained in detg. the relative rates

of vulcanization, tensile strengths and elongation of cured reclaims, depending upon whether they are cured with S alone or with S, accelerator and ZnO. Further natural aging tests show that the hardening of reclaims is accompanied by a great increase in acetone ext. There is, however, no relation between this and the behavior of the reclaims in cured rubber mixts.

C. C. DAVIS

The manufacture of air bags. R. THIOLLET AND G. MARTIN. *Caoutchouc & gutta-percha* 27, 14,962-3(1930).—Orange Vulcafixe R, an org. coloring agent, is shown by tests to be a satisfactory substitute for "golden antimony" in the manuf. of air bags.

C. C. DAVIS

Antioxidants. W. J. S. NAUNTON. *Trans. Inst. Rubber Industry* 5, 317-27 (1930).—A review and discussion dealing with features of general importance and interest, including certain new data. Certain antioxidants with no accelerating action delay scorching and overcuring with ultra-accelerators. Tests in this connection showed that the "set-up" of a mixt. contg. tetramethylthiuramdisulfide was retarded 30% in time by "Nonox." Certain antioxidants also protect cured mixts. against reversion (when the S is low). Chem. antioxidants are ineffective in cold vulcanized mixts. because their active groups are attacked by S_2Cl_2 , in which connection expts. showed that an antioxidant previously treated with S_2Cl_2 had no protective action in hot vulcanized mixts. Antioxidants do not cause fading of org. colors (cf. Garner, *C. A.* 22, 3804), and the apparent effect is a result of the added shade modifying the original color of the dye. If such a vulcanized rubber is exposed to sunlight, it acquires more nearly the color without the antioxidant, for the color from the latter fades faster than the dye. Tests of various mixts. cured to different states with diphenylguanidine and enough S to bloom, with and without "Nonox" antioxidant, showed that in all cases the antioxidant delayed or prevented blooming. Antioxidants retard the drying of oil varnishes, and this may be of great importance in the manuf. of footwear. Preliminary oxidation of "Nonox" antioxidant by H_2O_2 does not impair its antioxidizing properties, which renders improbable the theory that antioxidants are effective by virtue of a preferential absorption of O. Furthermore, a study of the effect of antioxidants on the O absorption curves indicates negative catalysis rather than preferential absorption (cf. Kohman, *C. A.* 23, 2600, 5610). There is, however, a slow irreversible reaction which gradually removes the antioxidant, as shown by the work of Rao on turpentine and pyrogallol (cf. *C. A.* 19, 1928). The slight antioxidant effect of reclaimed rubber may be due to an increased dispersion, for a chem. examn. of reclaimed rubber and its various exts. failed to show any substance with antioxidant effect. If combination of rubber with O is incidental to deterioration (as chem. combination with S may be incidental to vulcanization), then so-called antioxidants could better be called "anticollopotropes" (agents which oppose any change in the colloidal state of rubber). **Discussion.** *Ibid* 328-35.—An antioxidant was heated with S (twice the wt.) for several hrs. at 150° and was then compared in rubber with the same antioxidant not so treated. There was no difference in the antioxidant activity, indicating that antioxidants do not decomp. during vulcanization. In hot vulcanized mixts. some antioxidants protect against the detrimental effect of Cu, but not in cold vulcanized mixts. Antioxidants in rubber do not in all cases retard the drying of oil varnishes on the rubber. S_2Cl_2 is the only known substance which prevents the action of chem. antioxidants, and, therefore, the latter are effective only when used externally after pretreatment of the surface. In comparative tests where in one case an antioxidant was added to mixts. before S_2Cl_2 vulcanization and in the other case the surface of the cold cured rubber mixts. was treated with the antioxidant in $EtOH-C_6H_6$, the mixt. contg. the antioxidant deteriorated badly in 2-3 days in a hot oven, whereas the mixts. contg. no antioxidant but surface treated remained good for 20-30 days. This was true of high- and of low-grade mixts.

C. C. DAVIS

Organic accelerators. II. FRED GROVE-PALMER. *Rubber Age* (London) 11, No. 1, 17-8(1930); cf. *C. A.* 24, 1763, 2915.—A general description of various types of accelerators.

C. C. DAVIS

Accelerator combinations. WEBSTER NORRIS. *India Rubber World* 82, No. 2, 53-5(1930).—A discussion of combinations to minimize scorching, enhance acceleration and accommodate curing conditions to the construction and size of the product.

C. C. DAVIS

Evolution of hydrogen sulfide from vulcanized rubber. EDWARD WOLESENSKY. *Bur. Standards J. Research* 4, 501-13(1930).—Vulcanizates were heated at different temps. (25° to the temp. of destructive distn.) in a current of N and the H_2S was detd. in the issuing gases. Nine rubber-S vulcanizates were tested after various treatments: (1) No treatment either before or after curing; (2) extd. with acetone after curing; (3) extd. successively with acetone, $CHCl_3$, hot alc. KOH, alc. AcOH, aq. AcOH, $EtOH$ and acetone; (4) the rubber before mixing extd. successively with hot aq. NaOH at

200°, 2% aq. H_2SO_4 at 200°, aq. NaOH at 200°, hot dil. aq. HCl, dil. NH_4OH and EtOH, and, after curing, with concd. HCl, hot dil. HCl, hot water, EtOH and acetone; (5) the rubber in latex form purified by the Pummerer aq. alkali method; (6) the rubber in latex form purified by the Pummerer method, vulcanized and then extd. with alc. KOH, water, EtOH and acetone; (7) hard rubber not treated; (8) hard rubber extd. with acetone, and (9) soft vulcanizates pulverized and kept 2 yrs. in darkness. In every case, H_2S was recovered, which indicates that all vulcanized rubber evolves H_2S at all times regardless of the conditions. In part and under some conditions for the greater part, this H_2S is split directly from the rubber-S compd., and not merely during vulcanization. This was shown by the evolution of H_2S when there was no free S or non-rubber components in the vulcanizate, and also by the fact that over 60% of the combined S in hard rubber was removed. The rate of evolution of H_2S increased with the temp. and with the proportion of combined S. Since decompn. to H_2S is continuous and since its rate at any temp. diminishes continuously, the rate of evolution of H_2S at any temp. or time depends partly upon the previous history and the condition of the vulcanizate, as is shown by the expts. Evolution of H_2S occurs during vulcanization, and it may cause addnl. unsatn., which will be nullified by the consumption of more S. This may explain the excess combined S above the theoretical proportion found by Stevens and Stevens (cf. C. A. 23, 3596, 5612). Without S, this unsatn. may allow addn. of O, and such replacement of S by O would cause fundamental changes in the phys. and chem. properties of the vulcanizate, as reflected in its aging. The evolution of H_2S also entails loss of H, a result of importance in the problem of regenerating new rubber from vulcanized rubber. The results of Fry and Porritt (cf. C. A. 23, 5613) on the evolution of H_2S from hard rubber are in general confirmed in the present work, though in the latter H_2S was evolved even in darkness.

C. C. DAVIS

Hot vulcanization (sulfur vulcanization) of thin-walled transparent rubber goods instead of the earlier method of vulcanization with sulfur chloride. RUDOLF DITMAR. *Gummi-Ztg.*, 44, 1452, 1454(1930).—A review of certain patents (cf. *German Patents* 413,470 (Feb. 5, 1921), 448,763, K 1.39b, Gr. 7 (Feb. 27, 1923); *Brit. Patent* 300,936, C. A. 23, 4102; D. and Mathiesen, C. A. 23, 4374).

C. C. DAVIS

Vulcanization with sulfur chloride. ERICH WURM. *Kautschuk* 6, 33-6(1930).—A general review and discussion.

C. C. DAVIS

Recently developed instruments for tire vulcanizing process. R. E. OLSON. *India Rubber World* 82, No. 2, 59-61(1930).—Illustrated.

C. C. DAVIS

Patents

Latex. SIEMENS-ELEKTRO-OSMOSE G. M. B. H. Fr. 669,275, Feb. 7, 1929. In the electroosmotic sepn. of particles traveling initially to the anode, particularly of latex, the process is started in the presence of compds. contg. principally multivalent cations, or colloids, so that the sepn. takes place at the cathode.

Concentrating rubber latex. RUBBER LATEX RESEARCH CORP. Brit. 316,006, July 23, 1928. Latex is concd. in the presence of hemoglobin and is then dried in an atm. of sub-normal humidity. The product is a cheesy concentrate or a dry non-coherent powder which may be redispersed or may be mixed with fillers and vulcanized. Dil. NH_3 is preferably used for redispersion.

Rubber. FRANCIS C. DYCHE-TEAGUE. Fr. 669,465, Feb. 11, 1929. A rubber compn. of low viscosity, industrially utilizable, particularly as filling materials for molded objects or dissolved in a solvent as a *paint* or *lac*, is obtained by treating rubber by grinding and oxidation so as to destroy its fibrous structure and afterward chlorinating to a 50-60% content of Cl.

Rubber. I. G. FARBERNIND. A.-G. Fr. 668,907, Feb. 2, 1929. A rubber pulp is obtained by adding cellulose ethers sol. in water or solns. of these either to natural or synthetic latex or substances of the nature of latex and pptg. by heating.

Rubber compositions. H. A. MORTON. Brit. 315,661, July 14, 1928. Antiagers and antioxidants for use in prepg. vulcanized rubber products comprise derivs. of hydrogenated glyoxalin, particularly substituted dihydroglyoxalins or tetrahydroglyoxalins or their salts (except salts formed from strong acids which in themselves have a deleterious effect), in the proportion of 1.0-1.5%. Various examples are given.

Rubber compositions. C. MACINTOSH & Co., LTD., and F. H. TOOP. Brit. 315,512, May 11, 1928. Waste rubber which has been vulcanized is shredded, combined with about 3% of rubber in aq. dispersion and with vulcanizing agents, fibers and fillers, molded and vulcanized without drying.

Liquefied rubber composition. HAROLD P. BUTLER. U. S. 1,746,142, Feb. 4.

A compn. which is suitable for use as a *coating material* comprises liquefied rubber (contg. substantially all the condensable products obtainable upon boiling crude rubber dissolved in a solvent such as benzene) together with pyroxylin, benzene and CCl_4 . An app. is described suitable for prepg. the liquefied rubber. Cf. C. A. 23, 2850.

Tacky rubber composition. MERWYN C. TEAGUE (to American Rubber Co.). U. S. 1,746,875, Feb. 11. An aq. rubber dispersion is mixed with NH_4 resinate or a similar easily decomposable "water-sol. compd. of a water-insol. ingredient" for imparting tackiness, and decompn. of the added compd. is then effected (as by heating); the portion rendering it sol. is removed, to produce a tacky product which is suitable for use as a cement in the manuf. of footwear.

Heat-plastic rubber composition. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,745,926, Feb. 4. A sulfonyl chloride deriv. of a cyclic hydrocarbon such as *p*-toluene-sulfonyl chloride is incorporated with vulcanized rubber scrap and a softener and the batch is heated (suitably to about 140°).

Preserving rubber. JAN TEPPERMA (to Goodyear Tire & Rubber Co.). U. S. 1,746,371, Feb. 11. Vulcanization is effected in the presence of phenyl- β -naphthylamine.

Rubber products from aqueous dispersions. DUNLOP RUBBER CO., LTD., and G. W. TROBRIDGE. Brit. 315,814, April 19, 1928. In the manuf. of rubber articles from aq. dispersions by processes such as dipping, spreading or spraying, the deposition bases (which may be wholly or partly porous and may be formed of metal, glass or porcelain) are engraved, embossed, printed or otherwise colored with inks or the like to produce a corresponding marking on the products.

Rubber articles. HERMANN BECKMANN. U. S. 1,745,657, Feb. 4. The rubber particles of latex are aggregated to a stage of formation of a reticulous body, the inter-aggregate pores of which are of microscopically visible filter-size and occupied by the latex liquid (which may be effected by use of S and MgSO_4 or CaCl_2); a product suitable for use in filtration of liquids is obtained by curing this material (suitably by vulcanizing in water).

Lining tubes, pans and other articles with ebonite. H. F. W. MENZEL. Brit. 316,353, May 1, 1928. Mech. features.

Impregnating driving belts or other materials with rubber latex. P. H. HEAD. Brit. 316,335, March 29, 1928. The material is subjected to a vacuum in an impregnating chamber into which there is then introduced latex, which has been stabilized so as to prevent spontaneous coagulation at normal temps. and to facilitate penetration into the material; the impregnation is completed by use of pressure. Various details are described.

Finishing rubber goods with casein varnish. MAX N. NICKOWITZ (to E. I. Du Pont de Nemours & Co.). U. S. 1,746,162, Feb. 4. A casein varnish is applied to rubber articles such as rubber-coated fabrics and the varnished surface is then halogenated (suitably by a 4% soln. of Br in CCl_4) in order to produce a smooth pliable finish.

Coating surfaces such as metal or glass with rubber and like compositions. DUNLOP RUBBER CO., LTD., and E. A. MURPHY. Brit. 315,901, April 16, 1928. Hard coatings are formed by applying aq. dispersions of rubber or like materials and then heating (suitably to 150° for 6 hrs. under oxidizing conditions). Various details of compn. and procedure are described.

Apparatus for curing rubber tire flaps or other vulcanizable bands. DANIEL S. HARRINGTON (to Goodyear Tire & Rubber Co.). U. S. 1,746,699, Feb. 11. Structural features.

"Antioxidants" for rubber, etc. A. M. CLIFFORD (to Goodyear Tire and Rubber Co.). Brit. 316,251, July 26, 1928. Rubber or other org. materials such as transformer oils or soaps are preserved by the use, as an antioxidant, of an oily naphthylamine such as propyl-, butyl- or heptyl-naphthylamines. Various details and examples are given. Cf. C. A. 24, 1249.

Hard rubber varnish. WILLIS A. GIBBONS and THOMAS V. BINMORE (to The Mechanical Rubber Co.). U. S. 1,745,533, Feb. 4. Finely divided vulcanized rubber is mixed with boiling solvent naphtha b. $160-70^\circ$ approx. at atm. pressure and the mixt. is stirred until the rubber is dissolved; sufficient S is added to produce a vulcanized rubber having a combined S content of approx. 32% and the soln. and S are heated to approx. the b. p. of the solvent naphtha to produce a freely flowing hard rubber soln. contg. substantially no free S.

Rubber and like coatings. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 669,385, Feb. 8, 1929. Metallic surfaces are furnished with coverings or layers of rubber or like vegetable resins or substances resembling rubber by fixing to the surfaces a facing in cloth or thread and applying on the facing the coating materials in the state of solns. or aq. dispersions.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 315,356, July 12, 1928. Na hydride is used to effect the polymerization of butadiene hydrocarbons (suitably at temps. of 30–50°).

Artificial rubber compositions. I. G. FARBERIND. A.-G. Brit. 315,916, April 21, 1928. Finely divided carbon, metal oxides, silicic acid or like substances are added to artificial rubber or to initial material such as erythrene, isoprene or dimethylbutadiene before polymerization, in order to obtain an improved product on vulcanization. Examples with details are given.

Treating tire fabrics. FRANK L. SESSIONS. U. S. 1,747,533, Feb. 18. Thread or cord to be used for making tires is stretched up to approx. the knee of its stress-strain curve and the stretching stress is released before the material is embodied in a tire. This treatment serves to give improved uniformity and durability to the product.

Rubber vulcanization accelerator and preservative. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,747,186, Feb. 18. Rubber is heated together with S in the presence of a reaction product of piperidine and hydroquinone or other suitable compd. obtained by the interaction of an org. base and a hydroxy deriv. of benzene. U. S. 1,747,187 specifies the use of a compd. formed by the combination of di-*o*-tolylguanidine and stearic acid. U. S. 1,747,188 specifies the use of an aliphatic aldehyde deriv. of the reaction product of an aliphatic aldehyde ammonia and mercaptobenzothiazole, *e. g.*, the crotonaldehyde deriv. of the reaction product of $(\text{CH}_3)_4\text{N}_4$ and mercaptobenzothiazole.

Vulcanizing mold for pneumatic tires. PETER DE MATTIA (to National Rubber Machinery Co.). U. S. 1,746,107, Feb. 4. Structural features.

Apparatus for vulcanizing pneumatic automobile tires. ISADORE J. REMARK (to General Tire and Rubber Co.). U. S. 1,745,642, Feb. 4. Structural features.

Vulcanizing rubber. I. G. FARBERIND. A.-G. Brit. 315,554, June 22, 1928. A vulcanizing compn. to be added to natural or artificial rubber consists of a paste obtained by triturating a powd. compd. of S and Se with an oily or fatty material compatible with rubber, such as petrolatum, stearic acid, oleic acid or wool fat.

Vulcanizing and curing rubber goods. HENRY R. MINOR (to Industrial Process Corp.). U. S. 1,746,357, Feb. 11. Articles such as rubber tubes in a mold within a closed chamber are heated by application of a heating medium such as steam to the exterior of the mold and are subjected to the direct action of a non-oxidizing curing medium such as CO_2 or N. A portion of the externally applied heating medium is withdrawn and utilized for reheating the inert curing medium; this withdrawal effects circulation of the remainder and greater transfer of heat to the mold. App. is described.

Rapidly vulcanizing coating material of phenolic rubber composition. TEIKICHI SATOW. U. S. 1,745,768, Feb. 4. Substantially equal quantities of a compd. contg. fusible phenolic resin 100, wood flour 70 and asbestos 40 parts and of a material contg. rubber 100, S 50 and MgCO_3 100 parts are heated together at a temp. somewhat below 170°; the material is then converted into a semi-liquid (suitably by admixt. with a solvent); a fibrous material such as cloth or paper is satd. with the semi-liquid and a surface such as a metal article is covered with the resulting material and it is heated in place in order to effect hardening.

Rubber. THE B. F. GOODRICH CO. Ger. 487,776, April 15, 1925. Rubber is treated with H_2SO_4 , org. sulfonic acids, acid chlorides or mixts. of these. Approx. 15% H_2SO_4 is used, or a corresponding amt. of the other substances, and the whole heated to 100°. The mass may then be rolled.

Rubber articles from latex, etc. DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 317,129, May 12, 1928. To avoid disadvantages due to the persistence of air or gas bubbles in dispersions, emulsions or solns. of rubber or the like during manuf. of articles by dipping, spreading, spraying or electrophoretic processes, fluid pressure is applied during one or more stages of the manuf.

Rubber compositions. LOUISE PESZYNSKI (NÉE CHAUMEAU). Fr. 669,568, Feb. 13, 1929. Fiber such as wool, silk, fur, etc., is incorporated in rubber either by adding it along with vulcanization materials or afterwards.

Rubber deposition. TOTO CO., LTD., J. L. BUCHANAN and S. P. SCHOTZ. Brit. 316,924, May 5, 1928. Elec. or other deposition of rubber is effected from latex which contains a lignone ext., *e. g.*, sulfite cellulose lye, such as may be prepd. as described in Brit. 229,002 (C. A. 19, 3018) and which also may contain various other added substances such as NH_4 persulfate, a metabisulfite, a polythionate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or $\text{Na}_2\text{S}_2\text{O}_8$ and viscose, S and ZnO which may be deposited with the rubber. The anode may be coated lightly with graphite and a porous screen may be used. Mention is also made of the use of molasses, starch and glue.

Electrodeposition of rubber. P. KLEIN (to Anode Rubber Co. (England), Ltd.).

Brit. 316,594, March 29, 1928. A concd. dispersion from which rubber is to be electrically deposited is preserved with a substance which does not yield gas at the anode or with an alkali in too small a quantity to form gas or is treated as described in Brit. 257,885 (C. A. 21, 3141) to reduce the OH ion content, or a c. d. is employed corresponding to a jump in potential not exceeding 1.7 v. at the deposition surface.

Latex. SIEMENS & HALSKE A.-G. Fr. 670,567, Feb. 28, 1929. Particles of a liquid, particularly latex, are sepd. by means of an a. c., the arithmetical mean value of which is zero. The effect is different according to the electrodes used, the best results being obtained with electrodes of Al or alloys of Al. Ta and its alloys are also good.

Anti-aging material for rubber. CLAYTON ANILINE CO., LTD., and R. ROBINSON. Brit. 316,761, July 20, 1928. A condensation product is formed from α -naphthylamine 1 and acetaldehyde 2 mol. proportions, preferably in the presence of an inert solvent such as methylated spirit.

Compounds for preserving rubber. CLAYTON ANILINE CO., LTD., and R. ROBINSON. Brit. 317,205, July 20, 1928. Products which retard the deterioration of rubber are obtained by treating an aromatic amine such as diethylaniline or dimethylaniline with a condensation product from an aromatic amine and an aliphatic aldehyde such as the acetaldehyde- α -naphthylamine condensation product described in Brit. 316,761 (preceding abstr.). Various details and modifications of procedure for prepg. the compounds are described.

Rubber-like substances. EDGAR W. HULTMAN. Fr. 670,766, Mar. 4, 1929. See U. S. 1,704,194 (C. A. 23, 2071).

Artificial rubber. I. G. FARBERIND. A.-G. Fr. 670,996, Mar. 6, 1929. Emulsions of diolefins, such as butadiene, for the production of artificial rubber are made by emulsifying together an aq. soln. of an emulsifying agent and a soln. of the same or a similarly acting emulsifying agent in a diolefin, the emulsion being then polymerized with or without homogenization. The emulsions have the diolefin or the water in the disperse phase according to the proportions. Examples are given. Cf. C. A. 24, 1546.

Synthetic rubber. I. G. FARBERIND. A.-G. Fr. 669,942, Feb. 16, 1929. The addn. of substances for vulcanization or other treatment of polymerization products of diolefins is made at a temp. below 60°. Cf. C. A. 24, 1250.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 317,030, May 9, 1928. Polymerization of hydrocarbons such as butadiene, isoprene or dimethylbutadiene is effected with addn. of finely divided or colloidal metal oxides such as those of Mn, Pb or Ag, in aq. emulsion alone or with the addn. also of a colloid such as albumin, soap, dextrin and saponin. Org. or inorg. salts also may be added, and the metal oxides may be produced in the mixt. from other compds.

Rubber vulcanization accelerators. W. SCOTT (to Rubber Service Laboratories Co.). Brit. 316,932, Aug. 6, 1928. Compds. formed by the reaction of 2,4-dinitrochlorobenzene with mercaptoarylthiazoles or their alk. salts or like compds., *e. g.*, the K salt of mercaptobenzothiazole, are used as accelerators, which act on suitable heating and do not cause premature curing during prevulcanization treatment of the rubber. Various examples are given.

Rubber vulcanization. I. G. FARBERIND. A.-G. Brit. 316,692, May 8, 1928. Vulcanization is effected in water in which is dissolved, as an accelerator, a salt such as Mg dibenzylthiocarbamate, Ca ethylphenylthiocarbamate, Na dibenzylthiocarbamate or the Ba salt of ethylhexahydrophenylthiocarbamic acid (the prepn. of which is described).

Vulcanization of rubber. I. G. FARBERIND. A.-G. Fr. 669,795, Feb. 18, 1929. See Brit. 315,554 (C. A. 24, 1766).

Vulcanization of rubber. THE NAUGATUCK CHEMICAL CO. Ger. 487,777, Jan. 26, 1922. The vulcanization is hastened by the addn. of a condensation product of an amine of elec. disson. const. between 10^{-12} and 10^{-8} and a satd. open-chain aldehyde with 2-7 C atoms. A Zn compd. may be added. Thus, rubber, ZnO, S and the condensation product of PhNH₂ and heptaldehyde are mixed and put in the vulcanizing press in the usual way.

Rubber. THE B. F. GOODRICH CO. Ger. 489,968, Oct. 31, 1926. Addn. to 487,776. Powd. rubber waste from vulcanizing processes is regenerated by heating it with an org. sulfonyl chloride (*e. g.*, *p*-toluenesulfonic acid chloride) and raw rubber, till a strong exothermic reaction sets in. A softening agent such as resin may be added. Examples are given in which the mixts. are heated for about 10 hrs. at 140°. Cf. C. A. 24, 2007.

Rubber. K. D. P., LTD. Fr. 671,415, Mar. 13, 1929. Rubber with microscopic pores is made by adding to rubber latex or the concd. product of rubber latex, before, during or after agglutination, albuminous products or disson. products of albumin, particularly casein.

Rubber. ÉMILE A. L. ROUXEVILLE and PAULINE A. M. ROUXEVILLE (NÉE CREUZILLET). Fr. 671,623, Mar. 18, 1929. Terpenic products such as those described in Fr. 639,726 (C. A. 23, 722) obtained by polymerizing turpentine and having the general compn. $(C_{10}H_{16})_n$, are used in rubber manuf. as they dissolve gutta-percha or rubber; they are vulcanized when mixed with rubber; and are viscous at ordinary temp. but become liquid when slightly heated.

Stabilizing latex. A. J. SOMER and R. B. R. WALKER. Brit. 318,717, July 30, 1928. Stabilization of latex is effected by adding a B compd. such as Na pentaborate or a mixt. of borax and H_2BO_3 which will give the latex a p_H of between 6 and 9.2. A small quantity of a germicide also may be added.

Rubber articles from latex. UGO PESTALOZZA (to Società Italiana Pirelli). U. S. 1,750,540, March 11. Latex is treated with sym. diphenylguanidine or other suitable aromatic disubstituted guanidine and subjected to local heating to the forming temp. at the surface at which the rubber is to be formed (suitably by a heated former) so as to produce a local thickening of the latex and formation of a layer of compact coagulated rubber. Cf. C. A. 23, 3828.

Rubber sheets from latex. PAUL KLEIN (to American Anode, Inc.). U. S. 1,750,177, March 11. There are added to latex org. dyes, the ultramicros of which exhibit a neg. charge in the state of hydrosol, and excess dye not adsorbed by the rubber particles is extd. by centrifuging; the rubber is then pptd. from the purified latex by electrophoresis upon an endless supporting surface having anodic properties and continually travelling through the latex, and the rubber sheet thus formed is detached from the supporting surface. App. is described.

Emulsions of diolefins for artificial latex or rubber manufacture. I. G. FARBENIND. A.-G. Brit. 318,296, June 1, 1928. Emulsions, which polymerize on standing or by moderate heating, are prepd. by separately dissolving, in β -methylbutadiene or other suitable diolefin and in water, substances which react to form emulsifying agents, and then mixing the 2 solns. together; e. g., a fatty acid may be dissolved in the diolefin and NH_3 in the water. Substances promoting polymerization or subsequent vulcanization, etc., also may be added. Various details are described.

Chlorinated rubber composition. CARLETON ELLIS (to Chadeloid Chemical Co.). U. S. 1,750,583, March 11. A compn. for making films or sheets or for coating and impregnating fabrics comprises chlorinated rubber, diethyl phthalate and camphor. Cf. C. A. 23, 1012.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 672,323, Mar. 29, 1929. Homogeneous deposits of rubber are obtained by electrophoresis by using as deposition baths a latex, the concn. of which is increased beyond that of the natural latex, by thickening or by the addn. of an aq. dispersion of higher concn. obtained by thickening latex or by the dispersion of rubber already coagulated. The bath should contain at least 50% of rubber. Cf. C. A. 23, 3376; 24, 1249.

Preserving rubber. GOODYEAR TIRE & RUBBER CO. Fr. 671,656, Mar. 18, 1929. See Brit. 309,161 (C. A. 24, 527).

Preserving rubber. W. L. SEMON (to B. F. Goodrich Co.). Brit. 317,786, Aug. 22, 1928. As antioxidants in vulcanized rubber and as agents retarding resinification and tack in raw rubber there are employed such condensation products of aldehydes and secondary aromatic amines as are resinous and are non-accelerators of vulcanization. Examples are given. Cf. C. A. 24, 989.

Rubber articles. L. DOROGI, I. DOROGI and DR. DOROGI ES TARSA GUMMIGYAR R. T. Brit. 318,740, Aug. 27, 1928. A templet for use in the manuf. of articles such as bathing caps from thin sheet rubber is coated with a layer of powd. material such as talc mixed into a cohesive paste with a liquid such as alc. and glycerol, so that sufficient of the compn. is left on the rubber after withdrawal of the templet to prevent sticking.

Rubber articles. VREDDP, LTD. Ger. 489,868, Sept. 18, 1927. A method of producing rubber goods by dipping a form into liquid rubber and drying the rubber layer is described.

Rubber articles from aqueous dispersions. B. DALES (to Anode Rubber Co., Ltd.). Brit. 317,435, Aug. 16, 1928. A base material such as metal, wood, glass or porcelain is dipped in, or otherwise treated with, a rubber dispersion and a coagulating liquid such as HOAc or a mixt. of acetone and formic acid (suitably successively and in alternate sequence to build up a layer of the desired thickness). A soln. in an org. solvent of the isomer obtained by the reaction between rubber and phenolsulfonic acid may be used, and various details of procedure are described.

Dispersing reclaimed rubber. REED P. ROSE and HAROLD E. CUDE (to Naugatuck Chem. Co.). U. S. 1,749,607, March 4. Reclaimed rubber is softened with

spindle oil, the softened rubber is plasticized as by mech. working and the plasticized material is subjected to mech. action in water contg. a water-sol. rosin soap until a smooth dispersion is obtained. U. S. 1,749,608 specifies mixing reclaimed rubber with an aq. emulsion of spindle oil and water contg. alk. sulfonated castor oil, until dispersion is effected.

Regenerating rubber. K. D. P., LTD. Fr. 671,278, Mar. 11, 1929. Vulcanized rubber is regenerated by mixing it with a peptizing agent such as glue, soaps, casein, gelatin or saponin and adding water.

Transferring designs to rubber surfaces. CALLENDER'S CABLE & CONSTRUCTION CO., LTD., and J. BOWYER. Brit. 317,620, July 27, 1928. Designs or markings are applied to paper or other suitable material (suitably in an ordinary copying ink with addn. of glycerol, gum or glucose) and the design is then applied to the rubber and the latter is vulcanized. $MgCl_2$ or $CaCl_2$ also may be added to the copying ink mixt. Details are given for applying a design to the rubber insulation of a cable.

Covering wheels and pulleys with rubber. ANODE RUBBER CO. (ENGLAND), LTD., and E. H. HEREFORD. Brit. 317,385, May 14, 1928. Rubber or similar material is applied from aq. dispersions by spreading, spraying, dipping or electrophoresis. Various fillers and other admixts. of auxiliary ingredients may be used. When coating is effected by dipping, a preliminary coagulating coating is applied which may comprise gelatin contg. $CaCl_2$ or $HOAc$. Various details and examples are described.

Internal coatings of rubber in pipes or other hollow articles. DUNLOP RUBBER CO., LTD., and W. H. PAULL. Brit. 318,435, June 12, 1928. Internal coatings are dried and prevented from sepg. from the article by circulation of a drying medium (such as air of low humidity) under pressure. Various details and examples are given.

Liner material for preventing adhesion of rubber. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,749,743, March 4. See Brit. 288,244 (C. A. 23, 732).

Bonding layers of rubber of different characters. HUGH C. LORD. U. S. 1,749,824, March 11. Bonding layers of different qualities are used together and each of these is of character corresponding to the adjacent material to be bonded.

Puncture-filling composition. BERT GARNER HARRINGTON and RHEINER SANDERS MASON. Ger. 491,351, Nov. 22, 1927. See Brit. 288,917 (C. A. 23, 731).

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 318,115, April 26, 1928. A diolefin such as isoprene is polymerized in the presence of an org. substance contg. H_2O_2 in loose combination such as the compds. of H_2O_2 with urea, betaine, KF, piracone or $NaOAc$. Various colloidal substances, buffers, emulsifying agents, etc., also may be added. Several examples are given.

Synthetic rubber. I. G. FARBERIND. A.-G. Fr. 671,272, Mar. 11, 1929. In the manuf. of synthetic rubber by polymerization of emulsified diolefins, the emulsions are homogenized before the polymerization.

Artificial rubber. I. G. FARBERIND. A.-G. Fr. 671,562, Mar. 16, 1929. Artificial rubber useful particularly as a soft rubber is made by polymerizing together dimethylbutadiene and isoprene or erythrene or the 3 hydrocarbons or their analogs or homologs as an emulsion in the presence of colloidal aq. solns. of albumin compds., emulsifying agents and other compds. of this kind. The products are vulcanized in the usual manner. Cf. C. A. 24, 2008.

"Rubber substitutes." J. W. MOUNSEY, W. T. GALBRAITH and H. G. BAILEY. Brit. 317,814, May 23, 1928. Seaweed 60 parts, treated with 2% HCl and washed with alc., is mixed with 60 parts of materials such as candleweed, desert milkweed, cactus juice, manila gum, gum arabic, gutta horfoot, Indian hemp gum, glue, fish oil, sunflower oil, bastard gum, shellac, neen insect gum, cativo gum, sharks eggs, gum chicle or balata, and this mixt. is added to an equal quantity of starch fermented with *Granulobacter butylicus* and *Bacillus orthobutylicus*. The mixt. is cooled and 5% of resin or fish oil and 15 parts of petroleum waste, gasoline, benzene, alc. and a soln. of S are added, followed, after 24 hrs., by addn. of a soln. of casein 3 parts in NH_3 soln., heating to 100° , cooling to 35° , addn. of milk of lime and then of CO_2 , a small proportion of oil, and further heating.

Vulcanized oils. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 672,503, April 4, 1929. Products resembling rubber are prepd. from unsatd. oils or oils contg. a considerable proportion of unsatd. components. The oils are emulsified with water, or other liquid not dissolving the oil, with an appropriate emulsifying agent and with or without a protective colloid or an alkali or both, then vulcanized by means of S, etc., and with or without an org. accelerator and an activating agent such as ZnO .

Molds for vulcanizing rubber. A. VOSHAGE. Brit. 318,129, Aug. 28, 1928. See Fr. 665,073 (C. A. 24, 989).

Rubber vulcanization and preservation. SOC. ANON. POUR L'IND. CHIM. À BÂLE.

Brit. 318,275, May 31, 1928. About 1% or less of compds. such as those used as described in Brit. 290,178 (C. A. 23, 1013) are used in making vulcanized rubber products to prevent ageing.

Vulcanizing rubber. DEWEY & ALMY CHEMICAL CO. Fr. 672,236, Mar. 28, 1929. Rubber is vulcanized by treating rubber latex dispersed in water directly with an active O vulcanization agent. The active O agent may be org. peroxides or NO₂ compds., preferably *sym*-C₆H₅(NO₂)₃. A protective colloid may be added to the latex.

Vulcanization of rubber. I. G. FARBENIND. A.-G. Fr. 671,733, Mar. 19, 1929. The vulcanization of natural or artificial rubber is accelerated by using as accelerators 2-mercaptoarylthiazoles, which are substituted in the C₆H₄ ring in the *o*-position with respect to the thiazole N by alkoxy groups, and which also contain other substituents such as halogen atoms, *e. g.*, 4-methoxy-6-chloro-2-mercaptobenzothiazole. Cf. C. A. 24, 2008.

Vulcanization of rubber. THE RUBBER SERVICE LABORATORIES CO. Fr. 672,458, April 3, 1929. Rubber is vulcanized by making a sulfur-rubber mixt. in a bath consisting of an aq. suspension of an ultra-accelerator practically insol. in water, with or without a stabilizer such as an alkali oleate. The accelerator is preferably a substance easily sol. in rubber such as a CS₂ deriv. of the reaction product of a secondary aliphatic amine (*e. g.*, a heterocyclic amine such as piperidine) and an aliphatic aldehyde (*e. g.*, CH₃O).

Rubber. ISTVAN DOROGI, LAJOS DOROGI and DOROGI & Co. GUMMIFABRIK A.-G. Ger. 491,723, Aug. 21, 1928. A mold for hollow rubber articles is coated with an easily removable layer of talcum, alc. and glycerol.

Rubber. MAX DRAEMANN. Ger. 492,740, May 8, 1926. The manuf. of fibers by forcing plastic rubber through nozzles is described.

Treating rubber latex. DUNLOP RUBBER CO., LTD., H. J. ALCOCK, ANODE RUBBER CO. (ENGLAND), LTD., W. L. UTERMARCK, J. D. SICKLER, J. A. BLICKMAN, J. F. DEWAL, N. W. SICKLER and AKTIEBOLAGET SEPARATOR. Brit. 319,410, April 26, 1928. Rubber latex, as soon as possible after being taken from the tree, is treated with 0.1-0.3% of NH₃ and then concd. by centrifuging. It may then be treated with NH₃ to bring the NH₃ up to 0.3-0.4% for transport or may be treated with other preservatives such as CH₃O. After transport, the concrete may be dild. with water or may have its NH₃ content reduced by blowing with air, subjection to reduced pressure or treatment with reagents such as CH₃O or acid. The rubber in the skim produced during centrifuging may be sepd. by coagulation with acid such as dil. H₂SO₄.

Coagulating rubber in latex. F. GABOR (to Anode Rubber Co. (England), Ltd.). Brit. 319,801, March 29, 1929. A substance coagulable by heat but normally having a stabilizing or "neutral" effect on latex, such as animal or vegetable proteins, albumins, or their degradation products, *e. g.*, hemoglobin or white of egg, are added to latex, and the mixt. is heated to 80-90° to cause the albumin to coagulate and the mixt. to gel. The material treated may be ordinary com. latex, which may have its alky. reduced, or may comprise various mixts. contg. rubber waste dispersions, resins, substitutes and cellulosic substances.

Latex containing dispersed factice. ALLEN F. OWEN (to Naugatuck Chemical Co.). U. S. 1,753,018, April 1. A material suitable for waterproofing fabrics, etc., is prepd. by dispersing factice in a water-miscible liquid and mixing the dispersion thus formed with an aq. dispersion of rubber.

Apparatus for spray drying of latex or similar materials. ERNEST HOPKINSON (to General Rubber Co.). U. S. 1,750,753, March 18. Structural features.

Rubber from guayule, etc. DAVID SPENCE (to Intercontinental Rubber Co.). U. S. 1,753,184, April 1. After harvesting and before treatment for extn. of rubber, plants such as guayule are treated with a stabilizing agent such as dimethyl-*p*-phenylenediamine to prevent deterioration of the rubber. U. S. 1,753,185 specifies extn. of rubber from guayule or similar plants, by mech. treatment in the presence of dimethyl-*p*-phenylenediamine or other suitable stabilizing agents.

Purifying gutta-percha and balata. A. E. PENFOLD. Brit. 320,209, Sept. 11, 1928. The raw product is shredded, most of the impurities are washed out with cold or cool water, deresination is effected with a solvent such as "petroleum spirit," a soln. is formed with a warm solvent, remaining impurities are removed by settling and the pure product is pptd. by cooling the soln.

Rubber deposition from aqueous dispersions. DUNLOP RUBBER CO., LTD., G. W. TROBRIDGE and E. A. MURPHY. Brit. 320,387, April 12, 1928. Shaped articles are formed by repeated dipping, spreading or pouring operations to form a plurality of substantially adhering fluid layers upon non-porous chemically inactive deposition strata and each fluid layer is dried (by heat applied to that side of the layer adjacent

the deposition strata) prior to deposition of the next layer. Hollow formers of glass, glazed porcelain, ebonite, Zn or Al may be used. Various details are described. Cf. C. A. 24, 1765.

Removing gases or volatile substances from rubber dispersions or emulsions, etc. E. B. NEWTON (to Anode Rubber Co., Ltd.). Brit. 319,344, Sept. 22, 1928. A neutral gas such as steam or air is blown through aq. dispersions such as artificial or natural lattices of rubber, gutta-percha, balata or emulsions of oil, wax, asphalt, etc., and suspensions of solids such as ZnO, silica, C black or S; *e. g.*, for the removal of NH_3 from preserved rubber latex. Non-volatile preservatives may be added to prevent premature coagulation. Various examples are given.

Rubber compositions. MERWYN C. TEAGUE (to Naugatuck Chemical Co.). U. S. 1,750,767, March 18. Substantially water-insol. wood distn. products such as acidic pine tar are neutralized, mixed with an approx. neutral material emulsified with a non-solvent, and the emulsion thus formed is further mixed with an aq. rubber dispersion to form a compn. which is stable and suitable for mfg. purposes. Cf. C. A. 24, 1764.

Rubber composition suitable for electrical insulation. FRANK S. MALM (to Western Elec. Co.). U. S. 1,752,531, April 1. A material which has stable elec. properties under sea bottom conditions is prepd. by solidifying and heat treating rubber in the presence of a salt soln. and in assocn. with a solid, natural, nitrogenous substance such as rubber proteins, followed by washing and drying; the heat treatment serves to render the nitrogenous substance sol. in water and the washing removes a considerable proportion of the solubilized material.

Coloring rubber. I. G. FARBENIND. A.-G. Fr. 673,981, April 25, 1929. Rubber is colored by pastes or aq. suspensions of dyes or colored lakes insol. in water. Cf. C. A. 23, 2851.

Preserving rubber. I. G. FARBENIND. A.-G. Brit. 318,865, Sept. 10, 1928. Vulcanized or unvulcanized natural or artificial rubber is preserved by addn. to the mixt. of an indene-phenol condensation products which may be obtained as described in Brit. 297,075 (C. A. 23, 2539), or a substitution product or salt of such a compd. An example is given of the use of the condensation product of indene and resorcinol.

Thermoplastic rubber derivatives. WEBSTER N. JONES and HERBERT A. WINKELMANN (to B. F. Goodrich Co.). U. S. 1,751,817, March 25. Products which are thermoplastic at relatively low temps. are prepd. by heating rubber (suitably at 160° for 15 hrs. with 10–20% of the salts in examples which are described) with salts such as AlCl_3 , AlBr_3 , AlI_3 , Sb chloride, bromide or iodide, Bi chloride, Cr bromide, FeCl_3 , FeBr_3 , FeI_3 , Fe_2I_3 , Mn iodide, SnCl_2 , SnI_4 , V chloride, Zr chloride, ZnCl_2 , ZnBr_2 or ZnI_2 . Products of different colors and degrees of resinous character or plasticity are obtained. Cf. C. A. 24, 265.

Ornamenting sheet rubber. ALFRED A. GLIDDEN and FRANK D. BEAN (to Hood Rubber Co.). U. S. 1,751,546, March 25. Sheet rubber is passed between a pair of calender rolls, one of which is pebbled, a powder such as starch is applied to the pebbled surface of the sheet, surplus powder is removed, and a design is subsequently printed comprising groups of parallel lines running at different angles to each other.

Transparent sheet material with alternate layers of gelatin and rubber. O. KLORTZ. Brit. 320,509, Sept. 24, 1928. Various details of manuf. are described for producing sheets with outer layers of gelatin and underlying or alternating sheets of rubber which may be formed from latex.

Forming joints in rubber articles by uniting portions of superposed rubber sheets, etc. VEREINIGTE GUMMIWAREN-FABRIKEN WIMPASSING VORM. MENIER-J. N. REITHOFFER. Brit. 320,451, Aug. 10, 1928. Mech. features.

Coating solid surfaces. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 673,447, Apr. 16, 1929. Solid surfaces such as metal or glass are coated with org. substances by applying a layer of a natural or artificial dispersion of rubber or vegetable resin and applying heat with exposure to the air till the layer becomes solid. Desiccation products such as oleates of Mn or Cu and vulcanization agents may be added to the dispersion.

Solvent-recovery apparatus for rubber-spreading machines, such as those used for coating fabrics. ERNEST A. ABELES. U. S. 1,752,875, April 1. Various structural details are described.

Extrusion apparatus for rubber-coating wires. GEO. H. SCHANZ (to B. F. Goodrich Co.). U. S. 1,751,844, March 25. Structural features.

Rubber-calendering apparatus. PARK E. WELTON. U. S. 1,751,116, March 18. Structural features.

Rubber articles. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 674,014, April 25, 1929. Non-porous heated molds are immersed in concd. aq. dispersions of rubber, etc., the total time of immersion in the dispersion being not more than that sufficient

to collect a sensibly fluid layer adhering to the molds, and drying. Cf. C. A. 23, 3828.

Hardening the surface of rubber articles. W. C. GEER. Brit. 320,427, July 18, 1928. The surface of golf balls or other articles is treated with a soln. of fuming SnCl_4 in ethylene dichloride or other suitable soln. in an org. solvent of a halogen salt of an amphoteric metal such as As, Sn, B, Ti, Fe or Al. This treatment may be followed by washing successively in ethylene dichloride and in alc. contg. NaOH or other alkali.

Rubber footwear. W. A. WILLIAMS and NORTH BRITISH RUBBER CO., LTD. Brit. 320,815, Dec. 24, 1928. The uppers of various kinds of footwear are formed of a material comprising a netted or open-work fabric, the meshes of which are closed by a waterproofing of transparent rubber.

Rubber floor covering material. M. M. DESSAU and S. L. FLORES. Brit. 319,416, July 31, 1928. A layer of rubber is united to a backing of sheet cork by vulcanization (without the intermediary of rubber soln.). Various details and modifications are described.

Golf ball covers. A. E. PENFOLD. Brit. 319,910, Sept. 10, 1928. Golf ball covers formed of gutta-percha or the like, with or without addn. of rubber, are molded and applied to the core in the presence of a comparatively low percentage or residue of solvent so that shaping under pressure may be effected at temps. which will not damage the winding of the core. Various details are given.

Rubber cement. LEON J. D. HEALY (to Fisk Rubber Co.). U. S. 1,752,557, April 1. A cement which is suitable for temporary attachment of various materials is formed from degraded crepe rubber 12, a rubber solvent such as gasoline 87.5 and colophony 0.5%.

Rotatable drum apparatus for drying granulated reclaimed rubber. ALFRED T. OAKLEY and PAUL LUPKE, JR. (to Essex Rubber Co.). U. S. 1,750,813, March 18. Structural features.

Heated rotary drum apparatus for regenerating vulcanized rubber scrap. ADOLFO MRACH (to Soc. italiana pirelli). U. S. 1,754,177, April 8. Structural features.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 320,362, March 30, 1928. Isoprene is obtained from natural carbonaceous materials such as coal, brown coal, distn. products such as tars, also "mineral oils and similar bituminous products" and natural gas by converting the initial materials into C_2H_2 (either directly or with intermediate formation of CH_4), converting the C_2H_2 to AcH , polymerizing to form aldol, reducing to form 1,3-butylene glycol, partially dehydrating to form methyl ethyl ketone, condensing with CH_2O to form methyl (2) ketone (3) butanol, reducing this to 2-methyl-1,3-butylene glycol and dehydrating the latter to produce isoprene (which may be polymerized to obtain a synthetic rubber). Numerous details of the successive steps of procedure are described.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 320,960, April 26, 1928. Diolefins are polymerized in the form of emulsions in the presence of H_2O_2 and substances such as Carragheen moss, gum arabic, molasses or linseed meal; other substances favoring polymerization also may be added such as emulsifying agents or substances modifying the surface tension such as amyl, heptyl, benzyl or other alcs., electrolytes and buffer substances. Examples are given.

Improving the "aging properties" of rubber on vulcanizing with sulfur. HERBERT A. WINKELMANN (to B. F. Goodrich Co.). U. S. 1,751,848, March 25. Before vulcanization, there is added to the rubber mixt. a blown product of the distillate residues of petroleum capable of producing a blown product having a softening point of about 150° and a penetration at 50° of between 8 and 16.

Vulcanizing rubber. STANLEY J. PEACHEY and ALLON SKIPSEY. Ger. 488,208, Nov. 17, 1925. See Brit. 242,464 (C. A. 20, 3842).

Vulcanizing sheet rubber. C. MACINTOSH & CO., LTD., and H. C. YOUNG. Brit. 319,448, July 27, 1928. An app. is described, in which the sheet rubber is passed between an endless belt and a drum, the weight of which serves to produce at least part of the pressure which is applied to the sheet.

Vulcanization of rubber. I. G. FARBENIND. A.-G. Fr. 673,845, April 22, 1929. Liquid derivs. of guanidine such as pentamethyl- or pentabutyl-guanidine are used as accelerators in the vulcanization of natural or artificial rubber. Cf. C. A. 24, 2330.

Rubber vulcanization. ADRIEN CAMBRON (to Roessler & Hasslachler Chem. Co.). U. S. 1,754,010, April 8. Accelerators are used comprising a product obtained by reacting, under substantially anhyd. conditions, and in the presence of a small quantity of acidic material such as ZnCl_2 and HCl , a primary aromatic mono-amine such as aniline or xylidine contg. not more than 2 methyl groups attached to the benzene nucleus and an aldehyde such as crotonaldehyde or acetaldehyde or butylaldehyde.

Rubber vulcanization. I. G. FARBENIND. A.-G. Brit. 320,699, July 26, 1928. Vulcanization of natural or synthetic rubber is effected with an addn. of an org. deriv.

of NH_3 in which at least one H of the NH_3 is substituted by an olefinic radical, *e. g.*, 1% of butenylpiperidine, methyldibutenylamine, methylbutenylamine, the reaction product of mercaptobenzothiazole and butenylpiperidine, thioglycollic N-*n*-amylenylamine, and the reaction product of vinyl acetate and NH_3 . Cf. C. A. 24, 2008.

Machines for the continuous vulcanization of rubber. JEAN R. P. DESTRIEZ. Fr. 674,080, April 26, 1929.

Apparatus for vulcanizing inner tire tubes, etc. ROBERT MAYNE (to B. F. Goodrich Co.). U. S. 1,751,869, March 25. Structural features.

Vulcanizing tire treads to casings with an intervening rubber layer containing an electric heating resistance. W. B. BURKE. Brit. 320,558, Nov. 26, 1928. Vulcanization may be effected in wood molds while the tire is expanded by an air bag.

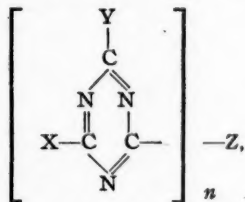
Purifying and concentrating latex. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,754,535, April 15. In prepg. concd. and purified permanent dispersions of isolated rubber latex particles, all suspended matter greater than 5 μ in diam. is removed and there is added to the latex an agent such as carrageen sol. effective to accelerate the sepn. tendency of the particles without increasing the coagulation tendency; the treated latex is subjected to a gradually increasing centrifugal force and the natural serum of the latex is displaced by a soln. contg. a protective colloid such as an ammoniacal soln. of hemoglobin and the concentrate is removed from the influence of the centrifugal force without violent agitation of the effluent. App. is described.

Concentrating latex. HENRY W. BANKS, 3RD (to U. S. Rubber Co.). U. S. 1,755,379, April 22. In treating aq. rubber dispersions, the state of aggregation of the rubber particles is repeatedly increased (as by adding gelatin or other suitable colloid) and water-sol. material is alternately removed (suitably by gravity on standing).

Concentrating rubber latex. ISADOR TRAUBE (to Naugatuck Chemical Co.). U. S. 1,754,842, April 15. Latex is brought into contact with org. colloids such as carrageen moss and allowed to sep. into 2 layers; the concd. rubber latex is applied to the surface of an org. colloid jelly such as gelatin and is allowed to become an adherent layer.

Rubber. I. G. FARBENIND. A.-G. Fr. 674,968, May 13, 1929. The resisting properties of the polymerization products of butadiene hydrocarbons not distg. without decomn. and of natural rubber are increased by carrying out the vulcanization of such products in the presence of resins or of alcs., ethers or esters of high mol. wt. The products described in Fr. 662,603 and 662,431 may be used.

Rubber. SOC. ANON. POUR L'IND. CHIM. A BALÉ. Fr. 675,785, May 27, 1929. The durability of vulcanized rubber is increased by using as antioxidants compds. of the general formula:



in which X and Y represent any groups, Z represents an atom of H or a radical bound to the atom of C of the cyanuric ring by means of N, O or S and n is a whole no. The compds. are obtained by substituting other groups for halogen in the compd. of the above formula where X, Y and Z are halogen and n is one.

Aqueous rubber emulsions. WM. B. PRATT (to Dispersions Process, Inc.). U. S. 1,755,890, April 22. Previously coagulated crude rubber is dispersed with soap and water, leaving the rubber in the form of globules of the size and shape of those of the original latex from which the crude rubber was derived. Soap and water are then sepd. (suitably by centrifuging) without coagulating the rubber globules. U. S. 1,755,891 describes the production of a non-sticky aq. dispersion, resulting from the manipulation of a coherent plastic mass of rubber with water and a colloid such as colloidal clay and contg. sepd. crude rubber globules which are difficultly or not at all coagulable with HOAc but coagulate on removal of water from the mass. U. S. 1,755,892 relates to dispersing rubber or rubber compds. by incorporating a water-carrying colloid such as sea moss into the mass, adding an aq. soln. such as an albuminate or gelatinate free from alkali and comprising a stable chem. compd. produced by combining a non-metallic colloid and a caustic alkali. Cf. C. A. 24, 264.

Rubber compositions. AMERICAN GLUE CO. Brit. 321,704, Aug. 10, 1928. See U. S. 1,683,862 (C. A. 22, 4274); Brit. 321,705. See U. S. 1,683,863 (C. A. 22, 4274).

Rubber conversion product. HERMAN A. BRUSON (to the Goodyear Tire and Rubber Co.). Can. 298,886, Apr. 1, 1930. A reaction product is formed by dispersing 10% by wt. of $\text{H}_2\text{SnCl}_6 \cdot 2\text{H}_2\text{O}$ in solid rubber and subjecting the product to a temp. of 130–150° for 2–5 hrs.

Derivatives of rubber. I. G. FARBENIND. A.-G. Fr. 676,287, June 6, 1929. New derivs. of rubber are made by the reaction of aliphatic or aromatic alkyl sulfo-halides or their substitution products with natural or artificial rubber, preferably in the presence of indifferent solvents. Examples are given of the treatment of rubber with phenylsulfonylchloride and *p*-nitrophenylsulfonylchloride.

Preserving rubber. I. G. FARBENIND. A.-G. Brit. 321,850, Dec. 3, 1928. Mold on rubber is prevented by treating the raw rubber with compds. such as a butylated naphthalenesulfonic acid, monomethyl sulfuric acid or Na dicresylphosphate (suitably in 10% soln.). Cf. C. A. 24, 2639.

Cleaning rubber. MARIUS A. V. CHARTRAIN. Fr. 676,194, June 5, 1929. Ketones and alcs. such as acetone and methylated spirits in which waxes or fatty substances are dissolved are used for cleaning rubber and like surfaces.

Coating materials with rubber. HEINRICH QUITTNER. Ger. 492,386, May 11, 1926. Paper and other fibrous, etc., materials to be coated with rubber are treated with latex to which a soln. or emulsion of shellac has been added. Thus, a mixt. of latex contg. 32–33% of rubber 1 with a 20% alk. soln. of shellac 6 parts by wt. may be used.

Rubber coatings by electrophoretic deposition and dipping. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 321,398, July 6, 1928. Articles with grooved, ribbed or corrugated elec. cond. surfaces are provided with a uniformly thick layer of rubber by electrophoretic deposition followed by dipping (or *vice versa*). The dispersions for dipping may be prepd. as described in Brit. 290,313 (C. A. 23, 1012) and the coated articles may be immersed in a dehydrating and settling bath as described in Brit. 303,544 (C. A. 23, 4596). The coated articles may be dried in warm air and further treated as desired.

Rubber-coated cords for fishing lines, etc. F. D. SMITH. Brit. 321,564, Nov. 15, 1928. Cords for fishing lines, nets and other purposes are formed of yarns coated with "fiberized rubber" prepd. by mixing cotton, asbestos or other fibers and rubber, gutta-percha or balata. Metal filaments also may be embodied in the cords.

Forming rubber articles by dipping. DUNLOP RUBBER CO., LTD., and G. W. TROBRIDGE. Brit. 321,913, May 19, 1928. A heated non-porous former is dipped into a concd. rubber dispersion only long enough for a substantially fluid layer to adhere to the former and is revolved to effect even distribution and then dried, stripped and the article is finished. Vulcanizing agents, accelerators, fillers, etc., may be added to the dispersion. Cf. C. A. 23, 547.

Apparatus for forming rubber strip by extrusion and covering it with fabric. FIRESTONE TIRE & RUBBER CO. Brit. 321,476, Aug. 17, 1928. Structural features.

Artificial flowers from sheet rubber. JAMES B. CROCKETT (to Cambridge Rubber Co.). U. S. 1,754,670, April 15. A sheet of previously formed rubber contg. vulcanizing agents and an "ultra-accelerator" is placed on a suitably shaped impression or form and vulcanized in applied position with but slight if any heating and at atm. pressure.

Device (heated by a gas burner) for shaping articles of hard rubber. FRANK FENTON (to Miller Rubber Co.). U. S. 1,754,993, April 15.

Preserving airbags. GERALD D. MALLORY (to Goodyear Tire & Rubber Co.). U. S. 1,755,069, April 15. Airbags such as those used in vulcanizing pneumatic tires have injected into them a soln. of glycerol contg. an inert pigment such as ZnO and asbestine and an oil such as pine tar, coal tar or tung oil which wets the pigment.

Apparatus for making annular tubes such as inner tubes for tires. HAROLD A. DENMIRE (to General Tire & Rubber Co.). U. S. 1,754,502, April 15. Structural features.

Apparatus for continuous extraction of moisture from rubber fiber by press rolls. FRANK L. FURBUSH (to C. G. Sargent's Sons Corp.). U. S. 1,755,214, April 22. Structural features.

Rubber printing rollers, etc. OXFORD VARNISH CORP. Brit. 322,621, Nov. 13, 1928. An outer layer of gum or roller compn. is carried on an underlying layer of sponge rubber. Various details of structure and manuf. are described. Latex and NH_4Cl may be used in producing the sponge rubber.

Composition for waterproofing paper, etc. ALBERT W. HOLMBERG (to American Rubber Co.). U. S. 1,754,827, April 15. An aq. dispersion of rubber is prepd. with an admixt. of an emulsion of wax and spindle oil.

Rubber substitutes. L. AUER. Brit. 321,726, May 4, 1928. Materials such as linseed, castor or fish oils are heated with modifying agents such as carbonates, sulfitcs, sulfides, thiosulfates or hyposulfites which form gases other than O (or with addn. of auxiliary substances which form such gases) and the modified product is vulcanized. Rosin or other resins may be added to prevent frothing, and various other details and modifications of treatment and use of auxiliary ingredients are described.

Butadiene polymerization products. I. G. FARBERIND. A.-G. Brit. 323,012, Aug. 17, 1928. Non-distillable polymerization products of butadiene or of its substitution products in which the 1- or 1,4-positions have been substituted with hydrocarbon radicals are heated, without S, to 100–500° to produce hard masses showing practically no extensibility. Before the heating, there may be added auxiliary materials such as solvents, rubber, polymerization products of other diolefins, fillers, coloring substances and plasticizers. The product may be hard, similar to ebonite and have good elec. insulating properties, or may be soft and pliable. Numerous details and examples are given. It may be used for making *molded articles, films, threads or coatings on metal or various materials.*

Butadiene polymerization products. I. G. FARBERIND. A.-G. Brit. 323,028, Aug. 17, 1928. The process described in Brit. 323,012 (preceding abstract) is modified by effecting the heat treatment in the presence of S, or substances supplying S, in a quantity less than that required for producing hard rubber from natural rubber; usually about 5% of S is employed. Several examples are given.

Rubber substitute. LOUIS LAURIN. Fr. 675,565, May 11, 1929. A rubber substitute particularly for tires is a compn. contg. bone glue 37.5, "colle de nerf" 12.5, salicylic acid 0.1, gum tragacanth 12.5, wood flour 5, water 125, glycerol 62.5, castor oil 7.5, colza oil 5, fatty soap 1.7, tallow 0.8, resinate 1.5, $K_2Cr_2O_7$ 1.5 and alum 2.5 parts.

Artificial rubber. JEAN BAER. Fr. 676,097, June 3, 1929. Sulfurized oils, particularly artificial rubber, are made by sulfurizing oils with the elastic substance obtained by the reaction of halogenated satd. hydrocarbons with polysulfides.

Artificial rubber. I. G. FARBERIND. A.-G. Fr. 676,007, May 31, 1929. Pastes which contain substances resembling rubber and which may be decomposed by water to give a liquid similar to latex are prepd. by concg. emulsions resembling latex or suspensions of substances resembling rubber in the presence of protective colloids such as oleate of Mg or Na. Cf. C. A. 24, 1546.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 322,114, Dec. 17, 1928. Diolefins in an emulsified form are polymerized in the presence of polymerized oils such as polymerized castor oil through which an oxidizing gas has been passed at high temp. or derivs. of these products such as are obtained by treating the polymerized or oxidized oils with NH_3 .

Synthetic rubber tire treads. I. G. FARBERIND. A.-G. Brit. 321,882, Aug. 30, 1928. Plastic products obtained by polymerizing butadiene, as described in Brit. 299,037 (C. A. 23, 3376) for making tires, is used for making the treads only.

Welding seams of sheet rubber. L. DOROGI, I. DOROGI and R.-T. DOROGI ES TARSA GUMMIGYAR. Brit. 322,572, Oct. 1, 1928. A method of welding by use of a hot tool and pressure, without use of an adhesive, is described.

Rubber vulcanization accelerator. WINFIELD SCOTT (to The Rubber Service Laboratories Co.). Can. 298,698, Mar. 25, 1930. An accelerator is formed by the reaction of equal mol. proportions of mercaptobenzothiazole and hexamethylene-tetramine.

Dispersed vulcanized rubber. WM. C. GEER and HARLAN L. TRUMBULL (to B. F. Goodrich Co.). U. S. 1,754,886, April 15. Vulcanized rubber is plasticized with the aid of a rubber softener such as kerosene or gasoline and the plasticized rubber is intimately mixed with a colloidal emulsifying paste such as may be formed from casein, Na_2CO_3 , artificial latex, water and NH_3 to form a relatively smooth paste-like mass, a non-solvent liquid such as water is added to the mass to form a non-viscous creamy liquid, and the latter is subjected to a comminuting action to reduce the size of the suspended rubber particles to approx. that of rubber latex.

Vulcanization of rubber. WINFIELD SCOTT (to The Rubber Service Laboratories Company). Can. 298,699, Mar. 25, 1930. A vulcanized rubber product is obtained by heating rubber and S in the presence of a vulcanization accelerator comprising a compd. obtained by treating a Schiff's base produced by combining substantially 93 parts by wt. of aniline and 72 parts by wt. of butyraldehyde with approx. 3 parts by wt. of butyric acid while simultaneously reacting and heat treating said Schiff's base with substantially 144 parts by wt. of butyraldehyde.

Vulcanizing rubber. I. G. FARBERIND. A.-G. Fr. 674,735, May 8, 1929. A reagent for the vulcanization of rubber contains natural or artificial rubber latex and Se or Se compds. in a very finely divided state, preferably colloidal.

Rubber vulcanization. PAUL I. MURRILL and WALTER W. EVANS (to R. T. Vanderbilt Co.). U. S. 1,755,703, April 22. A condensation product of aldol with diphenylethylenediamine is used as a retarder of deterioration. Other similar condensation products of aldehydes and diarylalkylenediamines can be used.

Rubber vulcanization. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,754,865, April 15. Vulcanization is effected in the presence of an accelerator formed by the reaction of acetaldo and one of the compds.: *o*-toluidine, *p*-toluidine, aminoxylene, aniline and benzylamine.

Vulcanizing tire tubes. FIRESTONE TYRE & RUBBER CO. (1922), LTD. Brit. 321,937, Aug. 17, 1928. App. and various mech. features of procedures are described.

Apparatus for vulcanizing inner tubes. EMIL SCHNEDAREK (to National Rubber Machinery Co.). U. S. 1,755,563, April 22. Structural features.

Apparatus for vulcanizing pneumatic tires. PETER DE MATTIA (to National Rubber Machinery Co.). U. S. 1,755,981, April 22. Structural features.

Vulcanized products from "isocolloids." L. AUER. Brit. 321,722, May 8, 1928. Materials contg. unsatd. acids of high mol. wt. such as drying oils, resins or mixts. of natural or synthetic resins, naphthenic acids, which have been treated by heating with alkali metals, their oxides or hydroxides, are vulcanized by treatment with S with or without activators such as ZnO or accelerators such as mercaptobenzothiazole, to produce a product which may be used as a *rubber substitute*. The reaction mass may be treated with radiations such as x-rays, or with gases such as O, N or CO₂, or alternately with H₂S and SO₂. The products may be emulsified with water. An example is given of the heating of rape oil *in vacuo* with KOH, followed by further heating with S, ZnO and triphenylguanidine.

Rubber compound. FRANK O. WOODRUFF (to H. H. Beckwith). Can. 300,002, May 6, 1930. Rubber-like coagulum is made by mixing latex with a quantity of drying oil approx. equal in wt. to the rubber in the latex, and adding to the mixt. a quantity of 40% CH₂O soln. equiv. to about 2% of the combined wt. of the oil and rubber in the mixt.

Rubber compositions. I. G. FARBENIND. A.-G. Brit. 323,322, Nov. 19, 1928. The strength of natural or synthetic rubber compns. is increased by the addn. of resinous esters such as those produced from glycols or ethylene oxide and colophony or abietic, phthalic or palmitic acids. Production of a transparent film, which is vulcanized with S chloride, is described.

Rubber compositions. I. G. FARBENIND. A.-G. Brit. 323,580, Oct. 18, 1928. Resinous or asphaltic oxidation products of high mol. org. compds. such as paraffin hydrocarbons and waxes or resinous or asphaltic conversion products of such oxidation products are added to natural or artificial rubber mixts. in quantities of 5-15% the wt. of the rubber, and the mixt. is vulcanized in a usual manner. Various details and examples are given.

Rubber composition for dry molding. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,756,411, April 29. A mass of filler material including fibers such as asbestos coated with unvulcanized non-tacky rubber from latex gelled *in situ* is used for making articles such as molded blocks or panels. Various details of prepn. are described.

Coloring rubber. I. G. FARBENIND. A.-G. Fr. 677,202, June 22, 1929. Natural or artificial rubber is colored by mixing in a grinder the colors in the powd. form with plastic or very viscous substances such as rubber factice to obtain a homogeneous mass which is afterward mixed with the rubber. Cf. C. A. 24, 2639.

Rubber sponges. CANOVE (SOC. ANON. DE NOUVEAUTÉS EN CAOUTCHOUC). Fr. 677,272, June 24, 1929. In the manuf. of rubber sponges substances liberating gases such as (NH₄)₂CO₃ as well as vulcanizing substances are added to rubber latex, which is then coagulated and heated. The crust formed is removed and the sponge is washed.

Forming tubes from rubber dispersions. DUNLOP RUBBER CO., LTD., G. W. TROBRIDGE and E. A. MURPHY. Brit. 323,519, July 6, 1928. The dispersion is coagulated or caused to set while on the inner surface of a rotating horizontal cylindrical mold. For thick tubes, the process may be carried out in stages. Various details are described.

Cord for use in rubber articles. WM. K. SAWYER (to Morgan & Wright). U. S. 1,756,069, April 29. A covering yarn is wound spirally around a central element such as a strand of yarn which is of only sufficient strength for resisting stresses incident to rubberizing and mfg. operations. Fabric formed from this yarn is rubberized and may be used in the manuf. of articles such as tires as a "breaker fabric."

Rubber conversion product. HERMAN A. BRUSON (to The Goodyear Tire and Rubber Co.). Can. 299,963, May 6, 1930. Ten % by wt. of H₂SnCl₆·2H₂O is dispersed in solid rubber by milling and the product heated to 130-150° for 2-5 hrs. A short heat treatment or low temp. gives a tough balata-like product, whereas a long

period of treatment or excessive temp. gives a hard ebonite-like substance. Cf. C. A. 24, 2916.

Cement for uniting rubber to metal. STEWART S. KURTZ, JR. (to the Goodyear Tire and Rubber Co.). Can. 299,954, May 6, 1930. A cement is obtained by mixing rubber dissolved in a rubber solvent with an inorg. salt of Cu or Co in a solvent that does not dissolve rubber. Cf. C. A. 23, 5353.

Utilizing old rubber. H. PLAUSON. Brit. 323,526, Sept. 6, 1928. In producing, from old rubber, dispersions suitable for *lacquers*, the old rubber is heated in a solvent such as benzene, other petroleum hydrocarbons, turpentine or tar oil, in the presence of a small proportion of an org. anhydride or peroxide such as acetic or phthalic anhydride or benzoyl peroxide (suitably in an autoclave with stirrers, at 160–180°). Asbestos or other coarse or fibrous material is sepd. by filtration and fillers may be further removed by sedimentation or centrifuging. Coloring materials may be added and the dispersions are suitable for *impregnating paper, pulp, leather*, etc. The heating may be effected in N or CO₂, and chlorinated hydrocarbons also may be used as solvents.

Films, threads, disks, etc. I. G. FARBERIND. A.-G. Fr. 676,658, June 14, 1929. Films, threads, etc., are made by treating the polymerization products of hydrocarbons of the butadiene series with sulfurizing agents such as S₂Cl₂ until the high elasticity characteristic of rubber disappears.

Polymerized hydrocarbons. I. G. FARBERIND. A.-G. Fr. 677,416, June 25, 1929. Hydrocarbons of the butadiene series are polymerized to synthetic rubber by treating them either cold or heated by NaH.

Linoxyn and artificial rubber. I. G. FARBERIND. A.-G. Fr. 676,659, June 14, 1929. In the manuf. of products of the type of linoxyn and artificial rubber, instead of the fatty oils generally used, unsatd. fatty acids obtained by the removal of water from the oxidation products of hydrocarbons of the paraffin series, or acids sepd. therefrom are used in the form of their esters with polyals. either separately or in mixt. with esters of other unsatd. fatty acids or with hydroxy fatty acid esters.

Rubber substitute. JEAN BAER. Fr. 676,475, June 10, 1929. See Brit. 314,524 (C. A. 24, 1545).

Accelerator of vulcanization. JAN TEPPEMA (to the Goodyear Tire and Rubber Co.). Can. 299,953, May 6, 1930. Certain salts of S-contg. compds., e. g., Na diethyldithiocarbamate or the Na salt of mercaptobenzothiazole, may be caused to react with such org. halogen sulfides as 2-benzoyl-4-nitrophenylsulfur bromide, to produce accelerators for vulcanization of rubber. Cf. C. A. 23, 1776.

Accelerator of vulcanization of rubber. JAN TEPPEMA (to The Goodyear Tire and Rubber Co.). Can. 299,952, May 6, 1930. Rubber is vulcanized by incorporating a reaction product of a mercaptobenzothiazole contg. basic N substituted in the aryl ring and diphenylguanidine into a vulcanizable rubber compd. and heating the mixt. thus formed.

Rubber vulcanization accelerators. WM. P. TER HORST (to Rubber Service Laboratories Co.). U. S. 1,756,315, April 29. Vulcanization is effected in the presence of an unsym. tri-substituted guanidine, e. g., ethylphenylphenylguanidine (the production of which is described).

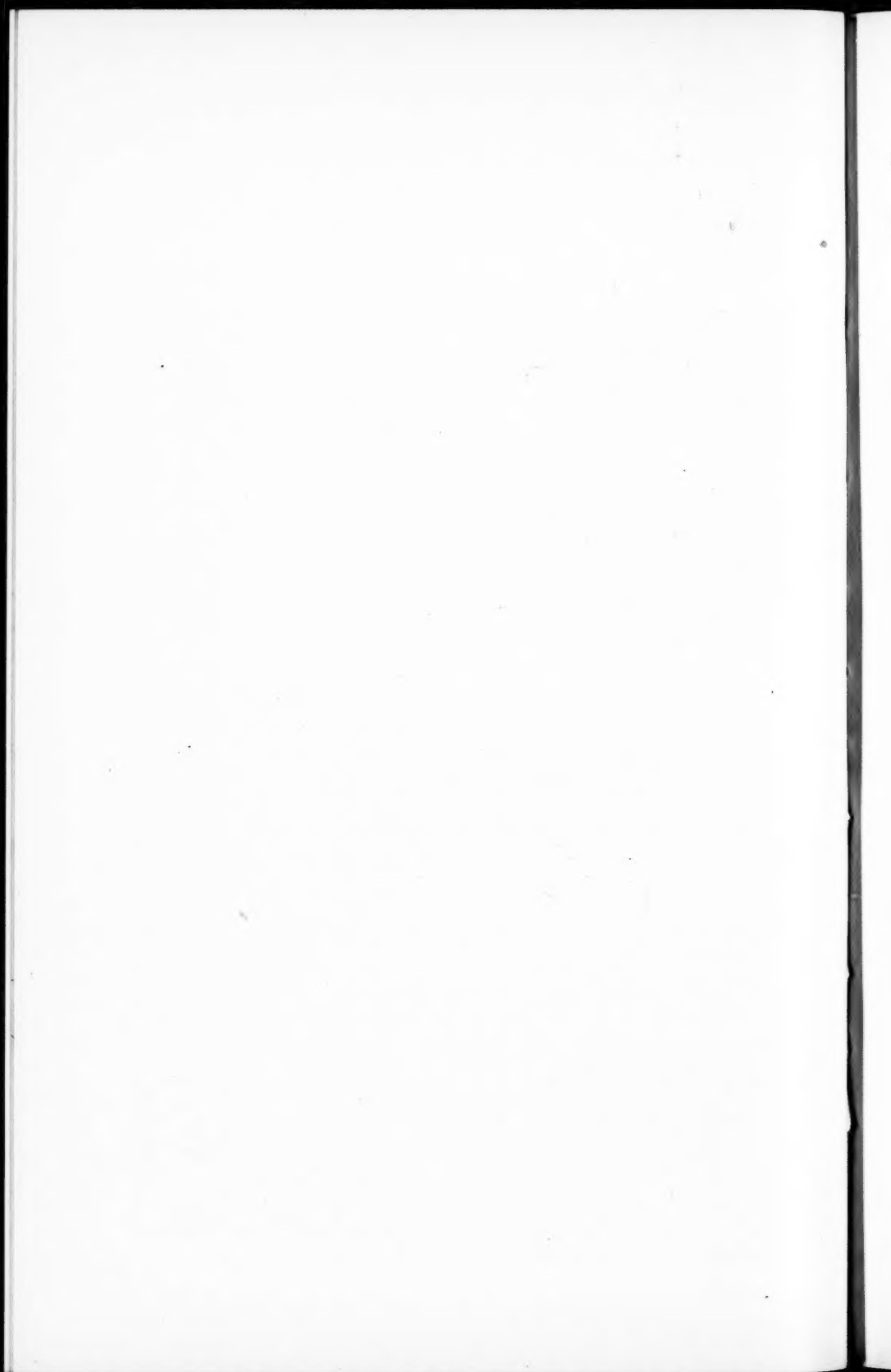
Rubber vulcanization accelerators. I. G. FARBERIND. A.-G. Brit. 323,512, Oct. 3, 1928. In the process for the manuf. of condensation products from α,β -substituted acroleins and aromatic amines described in Brit. 264,674 (C. A. 22, 186), org. or inorg. acids are used as condensing agents, and the products, with or without purification, may be used as vulcanization accelerators, suitably in admixt. with lampblack. Numerous details and examples are given. Cf. C. A. 24, 990.

Apparatus for molding and vulcanizing rubber articles. DUNLOP RUBBER CO., LTD., H. WILLSHAW and T. NORCROSS. Brit. 323,310. Nov. 10, 1928. Structural features.

Apparatus for vulcanizing tires. WALTER P. VOTH (to Akron Standard Mold Co.). U. S. 1,756,265–6, April 29. Structural features.

Vulcanizing rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,756,310, April 29. Vulcanization with S by heating is effected in the presence of an accelerator comprising the aldol deriv. of the reaction product of mercaptobenzothiazole with diethylamine or other suitable aldehyde deriv. of the reaction product of a mercapto compd. contg. a C—SH grouping with an aliphatic amine free from aryl substituents. Cf. following abstr.

Vulcanizing rubber. THE RUBBER SERVICE LABORATORIES CO. Fr. 676,786, June 17, 1929. Rubber is vulcanized by heating it with S in the presence of an accelerator contg. a reaction product of dinitrochlorobenzene with a mercaptoarylthiazole. The accelerator may also contain an org. base such as diphenylguanidine. A table of results with different accelerating mixts. is given. Cf. C. A. 24, 1546.



Some Engineering Problems in the Rubber Industry

H. C. Young

DUNLOP RUBBER CO., CHAS. MACINTOSH BRANCH, MANCHESTER, ENGLAND

It can be safely said that an industry such as the rubber industry produces by its horse power and its man power. Man power easily attracts most attention because its units are so easily seen, checked, and classed, and everybody considers themselves capable of directly controlling and eliminating such units. But thousands of horse power units rove all over our factories, idle and unemployed, except on work of distribution.

The man power is recorded even to habit units such as a boy or a girl, each has its own individuality; but the horse power units are considered only in droves, and whole groups are judged lost, whereas they are tearing out bearings, destroying gear teeth by wear, heating up cooling water, spoiling stock, and taking up man units to repair the damage.

It is interesting to note the rates of man power to H. P. in various industries:

	H. P. per Hour Workers
Rubber reclaim factory	5.1
Cotton mill	4.2
Chemical works	2.8
General rubber factory	1.02
Electrical manufacturers	
(Motors and electrical plant)	1.0
Without test bed	0.75
Automobile manufacturers	0.45
Boot trade	0.44

In a reasonable manner, these figures give the ratio of man power to H. P.

Comparing most industries with the rubber industry it will be found that whereas the rubber industry has most of its H. P. consumption centered in a limited number of large units, most other industries have instead a very large spread of H. P., such as a weaving shed in the cotton industry, where 1000 H. P. is taken up by many two or three H. P. loom motors. Another instance is to be found in a large engineering works, where the total H. P. is split up by motors, averaging about 20 H. P. each.

It is appalling when we consider the very low efficiency of any big unit in a rubber works, and it is amazing to note the complacency with which everyone surveys the situation.

A run-down chart or retardation chart on 500 H. P. mixing mill line will illustrate this. It is bad enough to start with a poor retardation chart on any piece of machinery, but it is unforgivable to allow—through lack of attention—wrong lubrication and generally poor maintenance. The run-down time is halved and the light load losses increase. The light load losses in a rubber plant are in the region of 30 per cent. of the full load losses, and comprise two main factors, transmission and friction losses, with such adjustments of the power factor as may be necessary by the aid of a static condenser or an asynchronous motor. Friction losses, however, are equally influenced by initial choice of electrical and mechanical plant and correct maintenance.

Why are we satisfied with ring lubricated bearings or grease cap lubrication for low speed journals when force lubrication is available or better still, when we can avoid either by the use of roller or ball bearings? A little calculation will show what it means.

Ring Lubricated Bearings

Friction losses at light load = 25%
Friction losses at full load = 50%

Ball or Roller Bearings

Friction losses at light load = 2.25%
Friction losses at full load = 5.0 %

Thus we get a reduction of 45% friction losses.

Then, again, many of our heavy machinery units should be put under the suspicion of circulating stresses much in excess of the stresses set up by input energy.

In 1926 the writer published a paper on this subject, and had in his support many eminent engineers. The theory was started by Lanchester, of motor fame, in considering the worm wheel drive for motor cars. He built a special apparatus to prove out this theory, and a paper was read on it before the Automobile Engineers of Great Britain. If you have an electrical generator supplying current to an electrical motor, you can circulate round such a circuit the full load of the units, and you need only have supplied to the circuit sufficient current to make up the losses due to windage friction and copper loss.

By this means therefore, a 1000 H. P. full load test can be performed by only drawing on an outside supply for, say, 100 H. P. and it is conceivable that you could burn out motor and generator by overload from a supply main incapable of supplying anything but a small portion of the overload current. A water turbine and a pump can be made to do the same thing, and in a single geared mixing mill, owing to the peculiar arrangement of the two rolls being linked by end wheels and having the mechanical circuit closed by a rubber blanket at the nip, a closed energy circuit is formed.

I estimate that four times the stresses considered present by calculating from the motor input are present, due to this closed mechanical circuit. This accounts for the excessive wear on the end wheel teeth of such mills, and also the very high pressures registered on the breaking bushes. These internal stresses circulating in a single geared mixing mill are much reduced in a double geared mill.

Invaluable help can be given to the rubber industry as a whole if a study is made of the pressures occurring in the bearings and on the face of the wheel and pinion teeth.

Gear drives in many of our primary plants are, to say the least, drives of convenience rather than well-thought-out engineering devices.

Everyone is familiar with the reproduction of the tooth pitch on the washing, mixing, warmer, and calender roll. On crudely designed machines, this can be measured by difference in diameter at the various adjacent points on a bow, but when the effect is so slight as to be observable by a light reflection only, and when no measuring instruments show a difference, it still points to a need in the design of the gears.

The conventional design of the plant, such as end wheel drives for mixing mills, gives no chance for a correct form of tooth to be employed.

Some years ago I rigged up a spectroscope to study end wheels on an 84" mill, and it was very intriguing to observe the remarkable variation in relative velocity between the front and back rolls of the mill. Very bad hunting between front and back roll was revealed. This is not to be marveled at when one considers that rubber is so lively that we can liken the operation at the nip of the mixing mill to that of compressing metal string through the nip. I was able to determine poor tooth design. The action was pronounced especially with an active bank on the

roll. From these observations I was induced to withdraw the end wheels on a 60" mill and, with different conditions of the nip, the front roll (which had of course no drive) was made to rotate in its usual direction, in the reverse direction or standstill. Unfortunately, I was never able to continue my observations, but one conclusion I came to was that the gear wheels on a calender had quite a lot to do with increasing calender grain, and that well-designed gears assist in the reduction of calender grain. This argument can be made plain by imagining a calender being driven with just pegs in the wheels instead of teeth, with the result that there was a very jerky movement of the rolls because they would be driven at varying velocities for a fraction of a revolution, depending on the number of pegs in the driven wheel. This varying velocity would of course be present at the nip. Therefore the rubber would be subjected to varying stresses which in turn would reveal itself in this case in the varying gauge of the calender stock. Reducing this down to a usual drive, it is not hard to imagine that the varying gauge gives way to varying initial stress, and in the direction of the calender grain.

Cooling devices used in the industry suggest a lack of attention given to the whole problem of cooling. It appears that stage by stage in the manufacture of the rubber, a critical temperature from room, plant, and material occurs, of which we know little and which nevertheless has some direct bearing on the efficiency and quality of the manufacture.

It will be conceded that the temperature of the washing mill room, mill, and rubber are in no way the same as that where fine calendered stock is being used. There must be a best condition in each case. It is under this consideration that our present design of plant reveals its lack of control. The use of the internal mixer gives us far better control than the ordinary two roll design. It gets away from critical temperatures at the nip, and enables us to take close observations.

It can be demonstrated that mastication is best attained at a controlled temperature, and that the heat added to the rubber must be taken from it as it leaves the mill nip. A saving of at least 30 per cent. power and 50 per cent. time is possible by so doing, and lower plastometer readings are possible for stocks such as sponge rubber or fine calendered sheet.

These figures can be obtained by special appliances on the mill, and by the aid of steel rolls. It is calculated that an 84" steel roll need not be more than $\frac{7}{8}$ " thick and still give reasonable deflection.

As an interesting point, hydraulic bushes, provided with an indicator, can be used as a means of measuring the plasticity of the batch. Such a bush fitted to the mill gives to the worker an indication whether the rubber is hard or soft after having been worked to the process time, and thus keeps to a better average plasticity reading than with a timed batch.

Cooling on a mixing mill needs much more study. The introduction of the internal mixer with spray cooling of the barrel is a big advance, but it seems to me that too few investigations are undertaken in the first place to determine the correct temperature the stock should be worked at. It is known at what low temperature the rubber will refuse to mix, and at what high temperature it will scorch, but little is known of the best temperature at which to mix. Yet there must be one. Many factories are now installing refrigeration plants, so that the circulating mill water is controlled to about 50° F., yet other plants are getting satisfactory results with similar mixing with a circulating water of 65° to 70° F.

The only possible answer here is that one mill is getting rid of its heat both off machine and batch externally quicker than the other, or the conditions in the nip are better.

In mill mixing, the temperature in the nip is the critical factor. I have known

mills giving a critical temperature at the nip as high as 125° C. with an average temperature of the batch at 105° C. This was with 4½" chilled iron rolls and cooling water of 60° F. With the same water, but by using a 2" steel roll, this was altered to 105° F. critical and 90° F. batch temperature.

The internal mixer has a distinct gain in this respect, as it altogether avoids a critical temperature. It will be agreed that most plant engineers and operating managers look to the mill cooling water as the means for taking away the unwanted heat during a batch.

The movement of air round a mixing mill, however, has a distinct bearing, particularly if the moisture content of that air can be controlled. Of necessity low velocity must be used, otherwise there is a waste of power, but as we know little about the actual temperature at which we must mix, only about the temperature at which we must not mix, it does not appear at this stage useful to go into closer reference. The internal mixer, again, has an advantage, since the control of temperature is so much easier.

Extruders leave much to be desired. Who yet knows the correct relation of barrel diameter to length—single, double, or three start thread—shape and volume of thread space for any given barrel—distance from end of screw to inside face of die—shape and volume of die box to barrel dimensions, and speed of screw? Should the screw have a varying pitch such as is used in cattle food extruding?

Types of stock have best extruding speeds and temperature in relation to cost and quality, and if the stock has a temperature rise in the extruding machine, all that has been suggested in the mixing mill must be applied to the warming plant. Is the point of critical temperature in the extruding machine at the point of packing along the barrel, or as the ropes of rubber are wound into the die box, or at the point of maximum slide in the die box itself? Some years ago I ran a number of colored mixes through an extruding machine, and after many hours the first color still lined the box, and each successive color was shown in layers in the die box rubber, the last added rubber being a core to all the preceding rubbers. The experiment clearly showed the relative movements between the wall of the box and the center point of the extruding.

The rate of production of the present extruder is very poor, and without fear of being challenged I believe it is the most inefficient and least understood piece of plant in any factory.

Calenders as we know them to-day need a lot to make them such a machine as we require them to be. It says a good deal for the calender man that he is able to work to such fine limits as are set him, with the whole army of variables with which he is supplied, to say nothing of the staff of critics he is surrounded by, few of whom are capable of anything but destructive criticism.

The study of the calender man is a study in itself. His physiology is quite apart from that of his fellows and it pays to study him as much as his machine. The industry would be in a sad plight if it was not possible to produce in the calender man the high degree of accuracy he attains.

We give him a 90" by 32" four-bowl calender and ask him to work this to 1/1000 tolerance with varying rubber stocks, varying cottons, and with a machine whose bearing clearance can often be measured with a jack knife, whose frame, bowl, and bearing have varying deflections responding to temperature, and pressure, and with clearance in the take-up gear giving no register. There is much to be done to make the calender a finished machine.

The bowl design is fundamentally wrong. It may be that it is limited by the material from which it is manufactured, but to attempt to regulate temperature through 8½" of cast iron seems a forlorn hope. If steel were used, this could be

cut down to at least $2\frac{1}{2}$ ", and it is possible to get down to 2". The Brinell hardness of the bowl face can be taken as 375 for steel as against 450 for chilled iron. If this latter hardness is really required, it is possible, when nickel-chrome plating becomes commercial for this size of article, that the bowl face will be hardened in that manner and, by the aid of a thinner bowl, cut out the tremendous time lag which prevails now.

Some calender makers actually supply a solid bowl calender for fine sheet for the bearings; their argument being that once the bowl is at the right temperature, it will stay there. All that can be said to this argument is "perhaps."

Until the calender is fitted with ball or roller bearings and all the slack is taken out of the adjusting gear, it cannot be looked upon as the last word. Moreover, the dimension of the nip must be put to stay and must be indicated, or an indicator visible to everyone must be included with such a machine. With the right temperature control the operator becomes less of a conjurer, and the product is more consistently and cheaply produced.

The deflection of the present calender bow has had little or no study. I cannot find anyone who takes what the turbine designer does, over-deflection. The turbine designer—if he did not exercise the greatest care in his calculations on deflection—would be in serious trouble with critical speeds. I believe it would pay to take even as great care in estimating the deflection of the calender bowl.

I was called in to give an opinion on a calender which it was impossible to run at correct speeds, and found that the trouble was due entirely to the deflection caused by the overhang of the large gear wheel.

The correct camber of calender bowls and the method of determining what this camber should be, is a closed book to many, and those who at present use a method, owing to their reluctance to disclose their method, are missing the help that a discussion would give.

Manufacturing methods from prepared stock, as apart from the methods of preparing the stock, need much more attention. Rubber flooring has definitely established itself as a good product. Unfortunately, it cannot compare in price with many of the floorings existing to-day, such as inlaid linoleum, although far superior in quality, service, and length of life.

Users are not plentiful because of high price. Cost of material is quoted as the reason of high cost—is this so? I do not know for certain what the raw material cost of linoleum is, but the direct labor cost per square yard is something like 4 cents, taking a quality at a dollar per sq. yard $\frac{1}{8}$ " thick. It is hard to believe that the material is much less than 80 cents, which is the cost of a similar rubber material. With the low production cost such as 4 cents per sq. yard for the wonderful designs the linoleum people produce, it is not astonishing they sell the finished article at so low a price as one dollar.

On the other hand, look what they have expended in money and mental and physical effort to attain that result. Their main machine costs \$250,000. One elector roll has 60,000 pins $\frac{1}{4}$ " square made up of 7 separate pieces, all true to less than one-half thousandth inch, and this accuracy is even greater in the operating gear. With a six-color machine, and a 20-ft. assembly drum, they have something like 1,200,000 pins, all accurately set to receive the pieces cut and placed by the elector pins. It takes 4 to 8 months to prepare an elector roll. They deserve all the success they have attained.

To my mind, we have to compete with brains, courage, and vision and not price.

As far as rubber flooring is concerned our effort in this line is very feeble compared with that of the linoleum people.

Rubber flooring lends itself to architectural design much more readily than any

other material. Brighter and more pleasing color schemes are possible with rubber. It therefore starts with certain initial advantages, added to which its physical characteristics are well in advance of most other materials. There appear to be only two main difficulties to prevent real bulk production.

1. Cutting without a distorted edge.
2. Curing at the same rate as the material can be produced.

Neither ought to be considered insurmountable. Freezing at the time of cutting might be the remedy for the first, and compounding with a specially constructed plant, for the second. This could be done by a curing machine consisting of a large rotating steam vessel giving a setting cure followed by a festoon heat chamber.

It seems that if appliances already existing in other industries were examined and considered, quite new ways of tackling the rubber industry problems would be devised. In the paper trade, an excellent interlocking device has been designed, whereby any number or series of operations can be synchronized to any speed, and held at that speed to within 0.01 per cent. If the first motion varies, all other operations move up or down with it.

1st operation.....	2% slow
2nd operation.....	1% slow
3rd operation.....	Key motion
4th operation.....	4% fast
5th operation.....	4% fast
6th operation.....	3% fast
7th operation.....	1% slow

Such a device is invaluable in paper making. For continuous calendering, in the rubber trade it could be made to be of great use.

Also for such work as proofing, cold curing, facing, and sweetening of proofed fabric, what help could it be for continuous manufacturing of rubber flooring?

The device is known as the Harland speed interlock, and there are, say, five operations separately driven in series, and running at different speeds. By means of differential gearing and electrical regulator, a definite fixing of the speed can be made within a very low limit of error. Each motor can be stopped, started, and made to crawl at will, in addition to being synchronized.

The manufacture of long length hose approaches something like a continuous production.

1. Mixing.....	10,000
2. Extruding core.....	2500
3. Braiding.....	300
4. Rubber ply.....	2500
5. Braiding.....	300
6. Extruding cover.....	2500

For a two-ply hose lead covering:

1. Curing.....	2000
2. Stripping.....	2000
3. Coiling.....	Unlimited

For these operations I have taken from a general average of various factories the speed expressed in feet per hour of the hose, and it will be seen that the out-of-balance speed is preventing the ideal being attained.

Is it beyond practical vision to imagine powder and drugs fed in at two places and cotton at another two, and no interruption taking place until the run is through? Something has to be done to the braiding machines before this can ever be obtained.

Wrapped hose manufacture looks all wrong.

Rubber hose has many advantages over steel pipes, and one advantage in par-

ticular is that the friction loss per foot run is lower with rubber than with steel. Careful tests have established this.

I give below the present costs of steel pipes and rubber pipes prevailing, and a further figure claiming reduced diameter for rubber because of its better carrying capacity. Can we ever get to really compete, and must we always use cotton?

STEAM PIPES

	1" Diam.	1 1/2" Diam.	2" Diam.
Steel	9.5 cents	15 cents	19 1/2 cents
Rubber	25 cents	34 cents	45 cents
Corrected diam.	5/8" = 16 cents	1 1/8" = 25 cents	1 3/8" = 34 cents

The present use of rubber on the silent block, pin joint, or bearing for motor cars, opens a new vision of the possible combination of rubber and steel.

I believe it will be found that in three types of factory something like the following occurs:

	Tire	General Rubber Goods	Garments
Motive power	60%	70%	50%
Process steam	24%	18%	30%
Heating steam	16%	12%	20%

When it becomes possible to do all our curing with boiling water, the ideal conditions will be attained.

Steam accumulators are being used to an increasing extent in Europe. In such plants as large steel works using steam hammers they have proved a great advantage, but the sudden overloading of the steam supply is not so usual in a rubber plant. It is questionable, however, if it would not pay to shut down the boiler plant for holidays and week ends and cure from a steam accumulator. This would also enable a certain amount of week-end curing to be drawn from it.

A certain manufacture in this country is carried on by heating water in a sealed circuit and a temperature of 500° is obtained. The water is never allowed to turn into steam, so sensible heat alone is present. This appeals to me as being a very efficient method.

One other thought on the use of steam. I believe it pays to examine each steam-using operation separately. The cost of metering for such a purpose is very great, but high cost can be avoided by placing a standard by-pass at those points where steam measurements are required, and one or two steam meters could be used, and any examination required made possible.

The coal bill in any rubber factory is a large item of cost. Unfortunately, there is not the correct balance of power, process steam and heating, to give ideal conditions. I suppose you must have studied the possibility of installing pass-out turbines, bleeding main turbines for process, exhaust heating, and their kindred, and have found that it is difficult to justify steam accumulators, but is it possible to obtain more ideal balance by better grouping? In nearly all factories there is latent heat to spare, and particularly so in the summer time, and every step made to reduce the mechanical horse power is a step toward the ideal balance. But would not a bolder method be to include some production needing a certain amount of low-grade waste heat, which could be taken from the power producers, and endeavor to design the production to this end?

A city power station in this country is selling steam for heating to a large area adjacent to the plant and also process steam to a rubber factory, while a large industrial concern is circulating condenser cooling water round an adjoining estate, for washing and bathing—a wide angle combination. Is it possible to include in a rubber works sympathetic production which would help to this end?

The Tensile Strength of Java Plantation Rubber

O. de Vries and R. Riebl

PROEFSTATION VOOR RUBBER, BUITENZORG, JAVA

In 1927 rumors were heard from different sides regarding a supposed decrease in tensile strength of plantation rubber.

These took such a form that *The India Rubber Journal* took the matter in hand and published a review¹ of data, furnished by different manufacturers and experts.

We gave a short review of figures for Java plantation rubber² for the years 1923-1926, from which no deterioration in tensile strength was to be seen; on the contrary, the figures showed a slight increase and the conclusion was that, at least for Java plantation rubber, there was no question of deterioration, as was to be expected for anybody conversant with methods of preparation on estates, which are more and more standardized and improved upon.

We are now able to supplement these figures with the averages obtained in routine testing in our station during the years 1927-1929. The figures are:

TABLE I

FIRST LATEX CREPE

Year	Number of Samples	Tensile Strength	Standard Time of Cure	Slope
1923	489	1.41	110	36.3
1924	561	1.42	109	35.8
1925	478	1.44	110	35.9
1926	561	1.45	110	35.9
1927	487	1.49	114	35.6
1928	464	1.51	107	35.6
1929	279	1.54	105	35.8

SMOKED SHEET

Year	Number of Samples	Tensile Strength	Standard Time of Cure	Slope
1923	263	1.42	109	37.2
1924	397	1.42	110	36.8
1925	247	1.44	111	36.9
1926	352	1.46	116	37.0
1927	386	1.48	120	36.8
1928	327	1.51	115	36.8
1929	229	1.54	114	37.0

These figures show a steady increase in tensile strength and no indication of any deterioration whatever.

Figures of a statistical nature, as the above, should, however, always be subjected to a severe analysis as regards the material from which they are composed; in our case the question might be raised whether in later years the number of estates from which samples were tested was large enough to make one sure that the figures are representative for the average properties of Java plantation rubber. It has been our well considered policy, since preparation was standardized some years ago by adopting adequate methods on practically all estates, to stimulate the regular testing of samples only in the case of estates wishing to go in for certificate rubber³ or of those purposely preparing uniform rubber of good quality; the rubber from other estates was only tested occasionally, as samples were sent in.

The objection could therefore be made that our figures for later years comprise only samples from a relatively small number of estates, and these among the best equipped ones, while small and backward estates were not represented at all or only rarely.

We therefore decided to study this question from another angle, and organized an inquiry into the properties of first grade rubber of as many estates as possible, collecting three samples (one drawn at random from the drying house, one from the stock being sorted in the go-down, and one from an already packed case) from as many estates as possible. In this way 599 samples of smoked sheet and 384 samples of first latex crepe from 293 rubber estates in Java and South Sumatra, large and small, were gathered and tested according to our usual method,⁴ using a 92¹/₂:7¹/₂ rubber-sulfur mixture. The average figures were:

TABLE II

	Number of Sets	Tensile Strength	Standard Time of Cure	Slope
Smoked sheet	203	1.52	111	37
First latex crepe	127	1.52	106	35

These values are in excellent agreement with the average values found in 1928 and 1929 (see Table I), and confirm our expectation based on knowledge of the conditions under which rubber is prepared on estates—that there is no question of a decrease in tensile strength or deterioration of another nature. The range of variability in tensile strength was as follows:

TABLE III

Tensile Strength, Kg./Cm.	Smoked Sheet		First Latex Crepe	
	No. of Sets	Per cent.	No. of Sets	Per cent.
1.4 ₅	1	0.5	3	2.4
1.4	34	16.7	18	14.2
1.5 ₅	88	43.4	47	37.0
1.5	61	30.0	41	32.2
1.6 ₅	17	8.4	18	14.2
1.6	2	1.0
	203	100.0	127	100.0

This variability, of course, is partly—to an unknown extent—due to the errors of determination for tensile strength,⁵ and only partly to real differences in the intrinsic quality of the rubber.

These figures having proved once more that the cry about a deterioration in tensile strength of plantation rubber is unfounded, the question arises how complaints could arise of a nature to make it desirable for *The India Rubber Journal* to draw special attention to them.

The inquiry held by *The India Rubber Journal* showed that the complaints were not general among manufacturers, but came from certain quarters. Several explanations offer themselves.

(a) Accurate testing of rubber requires great care and adequate equipment. Even public testing stations, using carefully chosen methods, know by applying a regular control (for instance, a standard control sample used for comparison in every test) that periods of difficulties occur, *e. g.*, lower figures for tensile. The cause of these deviations is not always known, but may be an irregularity in the testing machine (which, owing to wear, may run less smoothly) or a cutting knife that is not sharp enough, etc. We have experienced such periods in our own testing, and we have several times helped other institutes with control tests when they had trouble of this kind.

As testing methods in many (if not most) rubber factories are still surprisingly rough, deviating figures during certain periods are not unexpected.

(b) It seems doubtful whether all manufacturers are in a position to ascertain whether what they receive is real plantation rubber. The custom to make large blended lots, erasing the original plantation names, may well cause a not unimportant amount of rubber from small native and Chinese estates to sail under the name of plantation rubber and cause a decrease in properties for which European plantations are not responsible.

(c) In certain instances tensile strength seems still to be determined, not for a standard state of cure,⁵ but for a standard time of cure. A gradual change in rate of cure (which is of no real importance for intrinsic quality because it can be remedied by adjusting the mix, especially the accelerators) may cause the erroneous impression of a decrease in tensile strength.

It seems unnecessary to point out that manufacturers can guard themselves against deceptions by making sure that rubber from European estates only is used for those purposes where superior quality is a requirement.

References

¹ *India Rubber J.*, **74**, 809, 1082 (1927).

² *Ibid.*, **75**, 25 (1928).

³ *Ibid.*, **74**, 1081 (1927).

⁴ "Estate Rubber, Its Preparation, Properties, and Testing," by de Vries, 1920, pp. 452-530.

⁵ *India Rubber J.*, **74**, 809 (1927).

⁶ "Estate Rubber, Its Preparation and Testing," by de Vries, 1920, pp. 546-556.

The Coagulation of Hevea Latex

(Mrs.) N. Beumée-Nieuwland

In a publication by de Vries¹ a synopsis is given of the different theories concerning the coagulation of *Hevea* latex. de Vries comes to the following conclusion. Latex is a negatively charged colloid with a low degree of solvation. Positive ions can cause total or partial discharge. Flocculation follows, which is therefore caused by acids or metal ions. The heavy metals are strongest in this respect, and the alkaline earth and the alkali metals are less strong. As is shown by the author, these properties are not specific for latex, but they hold good in general for hydrophilic colloids.

Furthermore, de Vries has indicated that latex shows a phenomenon, the second liquid zone, which can be compared with the formation of zones in the flocculation range of colloids, which after flocculation emulsify again when the concentration of electrolytes is increased and which flocculate again when more electrolyte is added. Furthermore, attention may be called to the fact that the stability of latex as well as the stability of hydrophilic colloids can be decreased by heating.

The above facts led to the thought of looking at latex from a more general standpoint and of determining its place in the system which has been worked out for colloids.

Kruyt and Van Klooster² divide colloids into lyophilic and lyophobic colloids, according to their action toward the dispersing agent. They state the following differences:

(1) In the case of lyophilic colloids, flocculation takes place with high electrolyte concentration, whereas lyophobic colloids flocculate with very low amounts of electrolyte.

(2) In the case of lyophilic colloids the flocculation is reversible, whereas in the case of lyophobic colloids, the flocculation is irreversible.

(3) In the ultra-microscope lyophilic colloids only show a diffused light cone whereas lyophobic colloids show very well differentiated particles in lively Brownian movement.

(4) Lyophilic colloids (especially proteins) change their charge very readily. They are positively charged in acids and negatively charged in alkali, whereas lyophobic colloids usually have one specific electric charge which can be changed only by very specific means.

(5) Lyophilic colloids form systems, the physical properties of which are quite different from those of water (for example, viscosity), whereas lyophobic colloids form systems, the properties of which are very little different from those of water.

Latex as a Colloid System.—When investigating latex as a colloid system, one finds some properties which might make latex belong to the lyophilic colloids; however, one finds other properties, for example, the presence of distinctly visible particles in lively Brownian movement, which point toward latex being a lyophobic colloid.

The possibility exists, therefore, that in latex more than one colloid is present. In a system in which colloids of the above-mentioned two groups are present, the properties of one become predominant, and these are then called protective col-

¹ *Archief Rubbercultuur*, 8, 233 (1924).

² Kruyt and Van Klooster, "Colloids," 1928, p. 10.

loids. Hober³ states that this protective action takes place especially when hydrophilic and hydrophobic colloids are present at the same time. It is possible that the first one is adsorbed on the second one. However, in any case, the hydrophobic colloid is not precipitated but is protected from the usual coagulation agents by the hydrophilic colloid. Gelatin, protein, casein, dextrin, etc., are known protective colloids. Among the proteins the so-called euglobulins give the most protection, whereas the paraglobulins give less and the albumins least protection.

Protein in Latex.—In the *Archief voor de Rubbercultuur* (1927), page 323, one finds a reference by Ultée⁴ concerning experiments with the coagulation of "papaya" juice. Ultée states that coagulation probably takes place because the protective action of the proteins is eliminated. Several other authors have already pointed out the presence of protein in latex.

Removal of Protein.—(a) *Mechanically.* The question arose now whether it would be possible to remove protein preferably by non-chemical means. It has been recorded in the publication concerning cream from latex⁵ that ammonia latex on long standing shows a slow rise of the latex globules. This separation requires a very long time and does not yield a total separation by any means. A better separation is obtained by centrifuging the latex, which can be carried out in a way similar to that for milk. The latex cream contains considerably less nitrogen than the lower layer or serum; on diluting the cream again with water and on centrifuging again, one finds that the nitrogen content has decreased only very little, whereas on further washing the nitrogen content does not decrease any more.

Therefore part of the nitrogen compounds contained in latex can be separated by mechanical means. They remain partly in the lower layer, whereas the remainder is found in the centrifuge-sludge. The lower layer always contains a few per cent. of rubber; the ratio of protein to rubber, in other words the protein content of the rubber after coagulation, is much higher than with ordinary latex.

(b) *Chemically.* If one wants to remove the nitrogen compounds to a larger extent, then one has to resort to chemical means. It has been stated already in the publication on latex with much caustic soda⁶ that the nitrogen content of the rubber can fall to 0.03–0.01 per cent. by repeated washing of the latex with caustic. On acidifying the alkaline wash liquor, a gelatin-like precipitate is obtained, and after repeated washing with water, again dissolving in caustic, and again precipitating with acid, one finally has left a material which shows protein reactions (Millon's reagent, biuret, xantho-protein).

The protein which has thus been prepared from latex is soluble in very dilute alkali. On using a very small amount of alkali, all liquid is absorbed and a swollen mass is formed which does not liquefy until after a few days. This solution is very difficult to filter, and the filtrates are always slightly colored, opaque, and slightly cloudy. When acid is added to the mass until the latter reacts acid to litmus a precipitate is formed. If the solution is very dilute, then the precipitate is formed only slowly and is only visible after some time; however, if the solution is concentrated, a precipitate or sometimes a film can be seen on the spot where the acid falls into the solution; this precipitate disappears on shaking and is formed again when acid is added. This can be repeated until the whole liquid has obtained a certain acidity, at which point a film or a precipitate remains. Under the microscope the precipitate looks like a filament consisting of both fine and rough threads.

³ R. Hober, "Physikalische Chemie der Zelle und Gewebe," 1924, p. 287.

⁴ A. J. Ultée, *Teysmannia*, 28, 175 (1917).

⁵ *Archief Rubbercultuur*, 9, 371 (1925).

⁶ *Ibid.*, 9, 721 (1925).

On adding at once to the concentrated protein solution described above very dilute acetic acid, a precipitate is formed during a short time, which however redissolves promptly. The precipitate can only be formed again by adding strong mineral acid. On adding strong mineral acid directly to a concentrated solution of protein, a precipitate is formed which does not disappear on adding more acid. This precipitate consists of films and streaks. This protein is soluble in alkali. On precipitation with acid different zones are formed into which it may or may not precipitate, depending upon the acidity. Alkalinity retards gel formation, whereas acid promotes gel formation. This corresponds with the phenomena of the irregular series, as has been described for latex by de Vries.⁷ The occurrence of irregular series during the coagulation of latex is a phenomenon which is not specific for latexes, but which takes place with the lyophilic colloids. Graham has already given it the name of peptization, and apparently this is only a reversion process because that which was originally in solution is not the same as that which after precipitation dissolves again. Such phenomena take place with other colloids and with the proteins, not only on addition of acid or alkali, but also on addition of salts (see Porges and Neubauer, *Biochem. Z.*, **7**, 152 (1907)).

It is thought that the protein in the second reaction zone is not present any more as a molecule, but as an ion combined with the acid radical. This compound can dissolve partly in this acid environment and does not possess the properties of protein molecules any more. A combination with alkali can also take place. The protein then remains in solution, does not precipitate therefore, and does not form a gel. The more protein ions in a solution the more stable this solution is, and the smaller the tendency to flocculate. These so-called "acid and alkali proteins" require a higher temperature and a larger addition of alcohol than neutral protein in order to coagulate. The salting out effect which is reversible is of a higher order. In latex in the second liquid zone, one has therefore simply transformed the protein present into acid protein.

Besides the explanation according to de Vries, and to Belgrave, that in the second liquid zone the charge of the rubber globules be changed from negative to positive, it is also possible that the proteins are the carriers of the charge in the irregular series, so that in the second liquid zone the protein present in the latex has been transformed into acid protein. If this explanation is right, then alkali latex which has been washed and which is almost free from protein should not give a second liquid zone. This has actually been observed by us.

Concerning the presence of proteins in latex, several publications have appeared.⁸ Some investigators have pointed out that the protein does not at all have to be present as a film around each globule,⁹ though Hauser¹⁰ states, without any further evidence that "protein as is known is absorbed by the rubber particles in the form of a protective film ('Schutzhülle')." The protein can be present, for example, in the hydrosolic condition, the rubber globules being suspended in between. Results with centrifuging latex point in the direction that protein is present in this form and that it can be removed without necessarily having to change the globules. This would also be in agreement with the fact already observed by Arisz¹¹ that the nitrogen content of latex does not correspond to its rubber content. An emulsion is stable when the materials which surround the rubber globules are kept in such a condition that no coagulation takes place. It is known that the

⁷ *Versl. kon. Akad. Wet. Amst. afd. Nat.*, **32**, 45 (1923).

⁸ See literature referred to by Dr. O. de Vries in *Archief Rubbercultuur*, **8**, 233 (1924).

⁹ *Ibid.*, **8**, 233 (1924).

¹⁰ E. A. Hauser, "Latex," p. 78.

¹¹ *Archief Rubbercultuur*, **8**, 434 (1924).

quantity of the stabilizing agent to be added to latex is proportionate to the amount of latex, and not to the rubber content.

A similar example of protein protection is already known in the case of blood where the globules are present in an alkali hydrosol.¹² In the case of blood, globules can be washed (*viz.*, they can be freed from the surrounding protein by centrifuging). Now, in the case of latex, this can take place in the same way as has been described above, namely, by making latex cream. In the case of blood, one has to make use of a physiological salt solution in order to wash the globules, whereas when centrifuging latex, ammonia water is sufficient, though one can also use a physiological salt solution. When using water only, the apparatus sometimes clogs up. It is therefore advisable to add a little ammonia.

Microscopy of Latex Which Is Free from Protein.—When looking at latex under a microscope one sees that the globules move in a much less diffuse medium than is the case with ordinary latex. The same thing is observed with suspensions of latex which have been freed from protein by extraction with caustic. Both suspensions therefore have turned more lyophobic than the original latex.

Coagulation of Latex Which Has Been Freed from Protein.—The coagulation with acid of a suspension of latex which has been freed from protein either mechanically or chemically proceeds rapidly. A stiff coagulum is formed and sometimes the serum remains slightly cloudy. Both coagula can be rolled as usual and the fresh crepe behaves normally.

Changes in the Properties of the Rubber Made from Latex Which Has Been Freed from Protein.—(a) *Velocity of Drying.* The influence of the removal of proteins (and at the same time of other substances) is shown by the fact that the drying time has become much longer. It takes twenty more days with crepe made from cream, before the white spots disappear. Crepe made from caustic-treated latex becomes sticky and gummy and falls into pieces without becoming entirely dry (transparent).

(b) *Resistance to Tear.* A low resistance to tear is obtained in rubber made from latex cream or from latex paste which has been treated with caustic, or from rubber containing less nitrogen than normal.^{13,14,15} On the other hand, rubber from the lower layer, which contains more nitrogen, shows normal to good resistance to tear.¹⁶

B-Mixture from Latex Which Has Been Freed from Protein.*—Coagulation always takes place on adding acid to caustic-treated latex paste, which was diluted to a rubber content corresponding to that of ordinary latex and heated in the same way as is customary to make B-mixture. Therefore B-mixture cannot be formed. Latex cream does not form any B-mixture either (floculate). In the case of fresh latex the formation of B-mixture can be prevented by making the latex alkaline beforehand. These experiments will be reported on in a later publication.

Addition of Protein to Latex Which Is Free from Protein.—In order to determine the function of the substances which have been removed from latex with regard to velocity of drying and tendency to tackiness, experiments were started by adding some of these substances again to the latex. Portions of 50 grams each of washed caustic-treated latex were used. The first portion was diluted with an

* B-mixture is a latex prepared by running one volume of fresh latex into nine volumes of boiling water. (See de Vries and Beumée-Nieuwland, *Archief Rubbercultuur*, 8, 726-98 (1924).)

¹² E. Hekma, *Arch. Néerl. phys. de l'homme et des animaux*, 9, 67 (1924).

¹³ *Archief Rubbercultuur*, 9, 724 (1925).

¹⁴ *Ibid.*, 12, 566 (1928).

¹⁵ *Ibid.*, 10, 523 (1926).

¹⁶ *Ibid.*, 12, 564 (1928).

equal volume of water and then coagulated with 20 cc. of 10 per cent. acetic acid. To the second portion, one gram of casein was added, the mass was dissolved in 10 cc. of very dilute caustic soda, and then diluted with water to the same volume as the first portion and then coagulated with the same amount of acetic acid as in the first case. To the third portion was added double the quantity of casein; otherwise it was treated as the second portion. The three crepes obtained were all rolled and dried at the same time. The first one began to turn sticky after 14 days and after one month showed distinct tackiness. The second one also showed stickiness but not to the same extent as the first one, whereas the third was already dry after four days and did not show a trace of stickiness after four months.

In a second experiment we worked with five 300-gram portions of washed caustic-treated latex. Nothing was added to the first portion, three grams of casein were added to the second, six grams to the third, twelve grams to the fourth, and twenty-four grams to the fifth. The casein was, as in the first experiment, dissolved in very dilute caustic, then diluted with water and added to the latex suspension in such a way that finally all portions showed the same volume, including the first portion which was brought up to the same volume using water only. Coagulation was carried out with 10 per cent. acetic acid. After 48 hours the first coagulum was stiff, the second a little less stiff, the third portion gave a very thin coagulum, the fourth portion gave loosely combined flakes on top of a clear serum, which we pressed together and then rolled after syphoning off the serum. Also in the fifth portion the flakes had to be compressed before rolling could be carried out. The crepe from the fifth portion, the one containing most casein, was hard and brittle after two days of drying. The crepe from the fourth portion was less stiff and did not dry until after four days. The crepe from the third portion was normal to the touch and was dry in eight days. The crepes of the two other portions were not dry after 30 days and felt sticky.

Latex paste	300 cc.	300 cc.	300 cc.	300 cc.	300 cc.
Casein	...	3 gr.	6 gr.	12 gr.	24 gr.
Caustic 1%	0	1 cc.	1 cc.	2½ cc.	4 cc.
Water	300 cc.	300 cc.	300 cc.	300 cc.	300 cc.
Acid 10%	50 cc.	75 cc.	75 cc.	100 cc.	100 cc.
	(Crepe sticky)	(Somewhat sticky)	(Rather normal)	(Very hard)	(Very hard)

It seems that re-addition of protein to crepe is sufficient to restore the firmness and to prevent tackiness. For this latter purpose not all latex protein is necessary because it appears that the rubber from latex cream contains sufficient nitrogen (0.12%) not to be sticky. Rubber having a low nitrogen content as, for example, in the case of caustic-treated latex, always turns tacky.¹⁷ Rubber prepared according to Pummerer¹⁸ also turns entirely tacky.

The Hydrogen Ion Concentration during Coagulation.—Considerable agreement is found with a few proteins when one compares the p_H at which latex coagulates and the iso-electric point of several proteins. The iso-electric point of colloids is the point at which the disperse phase is zero and at which, therefore, the ion movement is also zero, and at which point the colloids show the greatest tendency to flocculate. In the case of proteins the iso-electric point usually corresponds to the minimum of flocculation. The iso-electric point has been determined for different proteins. For albumin this is at a p_H of 4.7, for globulin at 4.5, and for fibrinogen still closer to the neutral point.

¹⁷ *Archief Rubbercultuur*, 9, 723 (1925).

¹⁸ *Ber.*, 60, 2125 (1927).

Bobilioff¹⁹ has found that the p_H of the latex in the tree varies from 6.2 to 7.0. The latex in the tree is therefore almost neutral. Hauser and Scholz and Van Harpen²⁰ have found similar values. Coagulation starts at a value of approximately 5.0 and is therefore not far from the iso-electric point of proteins, which might indicate that coagulation is highly influenced by flocculation of proteins present in the latex. However, other factors also have their importance and proteins are not the cause of coalescence.

Further Considerations.—Belgrave²¹ in 1925 published his opinion that coagulation depends on the presence of a lipin complex and he found correlation with hemolysis.

In 1895 Overton²² published his lipid theory, which can be applied successfully to blood, and in my opinion this theory can also serve to explain many phenomena of the latex coagulation. A résumé of the theory is as follows: Before permeability, cells act as if they were surrounded by a lipid (fat-like) membrane. Lipid-soluble substances advance into the cell. Lipid-insoluble substances cannot enter. The membrane is not entirely lipid. One-third consists of other substances (protein).

This theory has been criticized from different angles. In the preface of the latest edition of Hober²³ the author thinks that all obstacles to his theory have been removed.

The lipoids include two large groups. One, the food lipoids and, second, the cytolipoids. The first group includes the neutral fats, the second group takes in the lecithins (phospholipoids), the cerebrosides, the phytosterols, the waxes, and the chromolipoids (see F. Czapek²⁴).

The occurrence of fatty acids in rubber, and therefore in the latex, has long ago been shown by Whitby.²⁵ The occurrence of sterol has long ago been shown by Whitby²⁶ and also by Dekker.²⁷

Already in 1923 Belgrave showed the occurrence of lecithin and cholesterol-like materials. Sterols belong to the higher alcohols and approach the plant waxes in some respects. As a rule they occur in the presence of fats and other lipoids (lecithins). The nucleus contains a polycyclic carbon grouping; they probably occur in every cell plasma in the form of fatty esters just like phospholipoids. However, the sterols are also closely related to the resin alcohols and sesquiterpenes from which they cannot be distinguished sharply, neither chemically nor physiologically.

The pure phytosterols are insoluble in water but soluble in warm alcohol, ether, petroleum ether, and in chloroform. In water they yield an opaque suspension which shows all the characteristics of suspension colloids. They have a double bond and swell strongly with water. They can also take up oxygen from the air, especially under the influence of light, in which property they correspond to the phosphatides. In that case the melting point changes, it becomes lower. The color reactions of the sterols disappear and the preparations turn yellow. Lifschütz,²⁸ who has experimented in this field, states that cholesterol is not nearly

¹⁹ *Archief Rubbercultuur*, **8**, 618 (1924).

²⁰ *Ibid.*, **8**, 46 (1924).

²¹ *Malayan Agr. J.*, **1925**, 373.

²² *Viertelj. Schr. Naturf. Ges. Zurich*, **40**, 144 (1895); 1899.

²³ Fifth Edition (1924).

²⁴ "Biochemie der Pflanzen."

²⁵ *J. Soc. Chem. Ind.*, **42**, 336T (1913); *India Rubber J.*, **70**, 382 (1925).

²⁶ *Ann. Rept. Brit. Assoc.*, **59**, 432 (1913).

²⁷ *India Rubber J.*, **70**, 815 (1925).

²⁸ J. Lifschütz, *Z. physiol. Chemie*, **50**, 436 (1907); **58**, 175 (1908).

as unreactive as is generally thought. Schulze and Winterstein²⁹ confirm this. Oxidation products (oxycholesterol and cholic acid) are formed which are similar to those obtained from blood.

Under the microscope the phytosterols show beautiful white plates or needles. They easily form esters with acid radicals; the ones with oleic acid and stearic acid are of physiological importance. They are not affected by caustic and they flocculate with acids. Undoubtedly they are very important substances which are found all over the vegetable kingdom in different parts of the plants. They are also present in the animal organism and are then called cholesterol. Some investigators prefer the name sterols for both, because the differences are only chemical. Czapek states that the dextro-rotating phytosterols usually form esters with fatty acids and the laevo-rotating form esters with cinnamic acid and benzoic acid.

Amyrin, a substance which has been isolated from elemi-resin, has properties which closely resemble those of the sterols. Czapek thinks that of all the sterols which have been isolated from rubber (?) one shows a remarkable resemblance to iso-cholesterol obtained from wool fat.

With regard to the occurrence of sterols in latexes, Czapek³⁰ states that lupeol is present in gutta-percha as the cinnamate and in jelutong as the acetate (Van Romburgh³¹). Sach and Tollens³² isolated alstol, alstonin, and iso-alstonin, which however, according to N. H. Cohen,³³ are lupeol and beta-amyrin. Cohen found beta-amyrin acetate and lupeol ester in balata. He also found beta-amyrin acetate and phytosterol in African rubber. Ultée³⁴ found beta-amyrin acetate, lupeol acetate, alpha-amyrin, and alpha-amyrin acetate in *Castilloa* rubber, and only beta-amyrin acetate in *Ficus* rubber.

Porges and Neubauer³⁵ published an important physico-chemical investigation on lecithin and cholesterol. Lecithin seemed to behave like an acid protein, whereas cholesterol acted as a suspension colloid. Lecithin can serve as a protective colloid for cholesterol. Cholesterol can swell strongly with water and can be precipitated with protein in a specific ratio, probably by forming a reaction product; Mond³⁶ found that protein can surround or protect lecithin particles even to such an extent that the iso-electric point of a lecithin emulsion which lies around a p_H of 2.3 (Rona and Deutsch later found 1.7) can be reduced with albumin to 4.7 and with globulin even to 5.3.

Rona and Deutsch³⁷ report as follows on the flocculation of cholesterol and lecithin suspensions. Cholesterol is flocculated at p_H 2.4 to 3.2. This suspension becomes more stable on the alkaline side and shows increasing flocculation on the acid side. Salts also cause flocculation in which case irregular series occur, the higher the valency of the flocculating ion the smaller concentration is necessary to cause flocculation. In the case of lecithin, a slow change of state of dispersion occurs to a great extent. It acts more hydrophilic than cholesterol. In the case of mixtures of the two, lecithin acts like a protective colloid for cholesterol even in very small quantities (0.0025%). They further state "these experiments give one the impression that the organism possesses, in addition to the specific structure

²⁹ Schulze and Winterstein, *Z. physiol. Chemie*, **43**, 316 (1904); **48**, 546 (1906).

³⁰ "Biochemie der Pflanzen," p. 800.

³¹ *Kon. Akad. Wet. Amst.*, **1905**.

³² *Ber.*, **37**, 4110 (1904).

³³ *Arch. Pharm.*, **245**, 236 (1907).

³⁴ *Bull. Jard. bot. Buitenz.*, [III] **5** (1922-1923).

³⁵ *Biochem. Z.*, **7**, 152 (1907).

³⁶ *Pflügers Arch.*, **197**, 574 (1922).

³⁷ *Biochem. Z.*, **171**, 89 (1926).

of protein as expressed by lecithin and cholesterol, to the changes of the hydrogen ions, and to the relationship of the separate electrolytes to each other, a finely balanced system which makes it possible to respond to disturbances by a change in physical condition. The organism is a much finer indicator and reacts on much smaller changes than our experimental methods do."

After having become acquainted with these publications, experiments were started in order to determine whether in latex similar substances might play a role. It was decided to try first whether B-mixture could be brought to coalescence by adding one or both substances. At that time we only had available animal cholesterol (obtained from wool fat). A one per cent. solution was made of this, and B-mixture was inoculated with increasing quantities. All flasks contained 50 cc. of liquid. After addition of the sterol, one cc. and one per cent. formic acid were added.

Control	10 dr. sol.	20 dr. sol.	30 dr. sol.	40 dr. sol.	50 dr. sol.	60 dr. sol.
After 1 day	After 1 day	After 1 day	After 45	After 51	After 1/2	After 1/2
liquid	liquid	coag.	min. coag.	min. coag.	min. coag.	min. coag.

It appeared therefore that B-mixture could be brought to coalescence with a crystalline substance from the animal organism. This fact is not especially peculiar, because Gerber has explained that, in Majorca, milk is boiled and then curdled by adding latex of a *Ficus* species or by simply stirring with a limb of *Ficus* in which a cross cut has been made. The use of *Ficus* latex, according to him, has been known from the "Odyssey" but has become obsolete, due to the fact that the use of rennet became known. In Sweden a small plant, the *Pinguicula* (family of the *Lentibulariaceae*) is used in order to make "thick milk." About these *Pinguicula*, it is known that this plant belongs to the same family as the *Utricularia* (Blaasjeskruid), known for its power to digest animal proteins.

Conclusion

In checking up as to which substances are present in latex, we find the following: protein, which can act as a protective colloid, lipoids (sterols, lecithin which can protect the sterol, esters of sterols), and further the contents of the globules, which is probably viscous. In view of the above considerations it is my opinion that one can picture latex as follows:

The rubber globules are suspended in a protein emulsion, and have a lipid wall and a viscous content. In the case of ordinary coagulation, where the p_H becomes 4.8, one might therefore form the idea that only the protein flocculated and formed a gel in which the globules stay put. Investigations by Rona and Deutsch have shown that the iso-electric point of lecithin is very much influenced by the presence of protein, and it is therefore probable that the lipid substances will be flocculated already at that lower p_H . When both protein and lecithin, the two hydrophilic colloids, are flocculated, there still remains the hydrophobic colloid sterol, which can easily be flocculated by the salts present. Then the contents of the globules are no longer protected, but stay included between the gels. The latter flocculation is irreversible and, therefore, once coagulation has taken place, inversion is impossible.

The Swelling of Latex

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In the course of investigations of the pure rubber hydrocarbon I had in view the preparation of an especially pure product in order to ozonize it and bring about a cleavage of the molecule. A great deal of work has already been carried on in the purification of rubber. The method of Harries in particular and also those of Pummerer give very fine pure products. Since, however, it was my object to obtain a preparation which was not produced by coagulation with acids, it was necessary to use a method which allowed the isolation of the rubber from a solvent. I recalled the experiment made by Harries¹ in Sicily in 1904 with latex from *Ficus magnol.* Borci and *Ficus elastica*. In order to determine if the rubber in latex already exists as such, Harries agitated fresh latex directly with ether, and he was able to obtain solid rubber from the ethereal extract without resort to coagulation. In a similar manner Hinrichsen and Kindscher² a few years later obtained a benzene solution of rubber from latex of *Kickxia elastica*. In none of this work, even in the earlier work by C. O. Weber and by de Jong and Tromp de Haas, is there any mention of the difficulties involved in obtaining the solutions.

For these experiments I used latex preserved with ammonia of the type which can be obtained commercially. This latex contained about 30 g. of rubber per 100 cc. of solution and was diluted about 5-fold. One liter of this latex thoroughly shaken with 1 liter of benzene gave a stiff jelly, instead of a solution of pure rubber in benzene. Only with great difficulty and with much loss was any rubber obtained from this jelly. Therefore benzene acted as a coagulating agent, whereas it usually serves as a solvent for rubber. As a matter of fact, a piece of solid rubber like crepe or sheet does not dissolve so very quickly in benzene. Even if the piece is cut up very fine, a considerable time is required to swell it. Only after swelling has taken place will it go gradually into solution. Does not some similar explanation account for the failure of my experiment?

In order to decide this question 25 cc. of highly concentrated latex was diluted with 10 times the volume of water and, in order to avoid coagulation, 25 cc. of strong ammonia were added so that there were in all 300 cc. of a dilute ammoniacal latex. On this liquid in a graduate was superposed cautiously, by means of a funnel, 200 cc. of benzene so that a very clear line of demarcation could be seen. The graduate was left standing at room temp. about 20° C. After two days a swollen middle layer of about 12 cc. was observed between the latex and benzene. Fig. 1 shows this swollen condition. By closer examination it could be seen that the upper boundary line in benzene was never a straight line, but instead appeared very wavy. Only rarely was it possible to make a tolerably satisfactory reading of the volume of swelling. In most cases the best that could be done was to estimate the value.

The graduate was observed for a longer period and the volume of swelling read

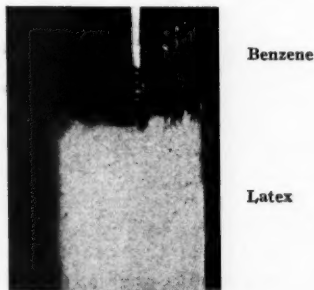


Figure 1

every other day. Table I and Figs. 2 and 3 give the course of the swelling in Experiment 11.

TABLE I

Day	Experiment 11 Swelling in Cc.	Day	Experiment 13 Swelling in Cc.
0	0	0	0
2	12	2	2
3	16	4	6
4	20	6	9
7	31	7	12
11	35	9	14
13	38	10	16
14	41	13	20
16	43	15	23
17	48	17	26
20	49	21	30
22	50	23	33
24	54		
28	58		
30	63		

Table I and Figs. 2 and 3 include a second experiment on swelling. This new experiment, called No. 13, shows an essentially lower curve of swelling. Perhaps

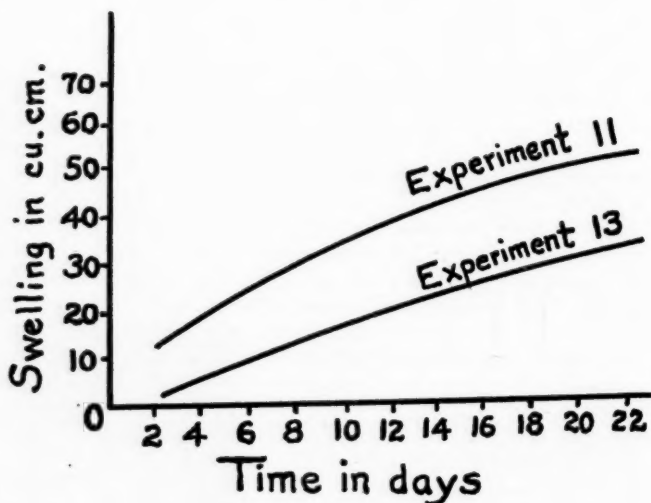


Figure 2

this remarkable swelling capacity of latex depends on its ammonia content. In order to ascertain this, I repeated Experiment 11 as Experiment 13, omitting however the 25 cc. of ammonia which was used in Experiment 11, so that the diluted latex contained only as much ammonia as was originally in the latex. The swelling began in Experiment 13 also but, as the curve shows, the volume of swelling was smaller. In Table II which follows I have grouped the concentrations of the individual components.

TABLE II

Experiment No.	G. Rubber per Liter	G. NH ₃ per Liter	Mol. NH ₃ per Liter	p _H
11	53.2	12.95	0.76	11.6
13	51.1	0.275	0.016	10.7

Though the concentration of rubber is a constant in both experiments, the concentration of ammonia changes in the ratio of 47:1. The p_H value decreases almost one unit. In this particular case I have had to abandon these experimental measurements, since E. A. Hauser has recently again emphasized that p_H -measurements of latex are carried out only with difficulty. I have considered it preferable to calculate the p_H value on the basis of the experimentally determined concentrations of ammonia in the latex and of the ammonia solution added. The equation used, which is easily derived from the Ostwald dilution law and from the law of mass action, reads:

$$[H^+] = \frac{K_{H_2O}}{K_{BOH}} \left(\frac{1}{2} \cdot \frac{\alpha^2}{1-\alpha} + \sqrt{\frac{\alpha^2}{1-\alpha}} \right)$$

Here $[H^+]$ = the concentration of hydrogen

K_{H_2O} = the dissociation constant of the water = 10^{-14}

K_{BOH} = the dissociation constant of the ammonia = 1.7×10^{-5}

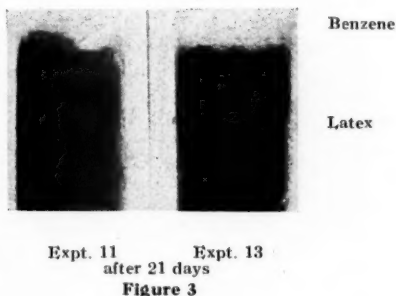
α = the degree of dissociation of the ammonia.

From this formula $p_H = 11.6$ for Experiment 11 and $p_H = 10.7$ for Experiment 13. The interesting fact appears also that ammonia favors the swelling of latex in benzene.

In addition to the experiments described above, I have tried still another series of similar experiments whose ammonia content lay between that of Experiments 11 and 13. The swelling curves lie correspondingly between the swelling curves of 11 and 13.

Something further might be added about these experiments, which may have a degree of probability. If the swelling in the individual experiments is plotted as a function of the p_H value, as shown in Fig. 4, it is evident that until p_H reaches 11.2 the swelling is almost constant, and only above the hydrogen number ($p_H = 11.2$) is there a relatively sharp increase in the swelling. Whether this visible minimum of the p_H at 11.2 really exists or is only apparent must for the present be left undecided. What can, however, really be regarded as certain is the pronounced rise of the curve in the more strongly alkaline medium. The swelling therefore increases with increase in the ammonia content.

The swelling of latex is of great interest in these experiments. However, here benzene also shows a remarkable phenomenon, which proceeds entirely parallel with the swelling; namely, a turbidity which increases with the increase in ammonia content. Figure 5 shows two samples, which were swollen for the same length of time, 21 days. The reaction of latex in Experiment 14 is $p_H = 11.5$, but in Experiment 15 it is 10.2. In Experiment 14 the benzene is completely turbid, whereas in Experiment 15 it is entirely clear. What the substances are which



cause this turbidity is still unexplained. In the ultra-microscope the benzene, strange to say, appears to be optically empty, and submicrons could be seen only to a minimum degree. Therefore it seems unlikely that the turbidity is caused by protein which, for some reason, migrated at a definite reaction into the benzene.

Moreover, no sedimentation took place from the turbid benzene, and the entire volume of benzene remained uniformly turbid. It is possible that here it is a question of dispersed water, for in graduates which have remained standing for a

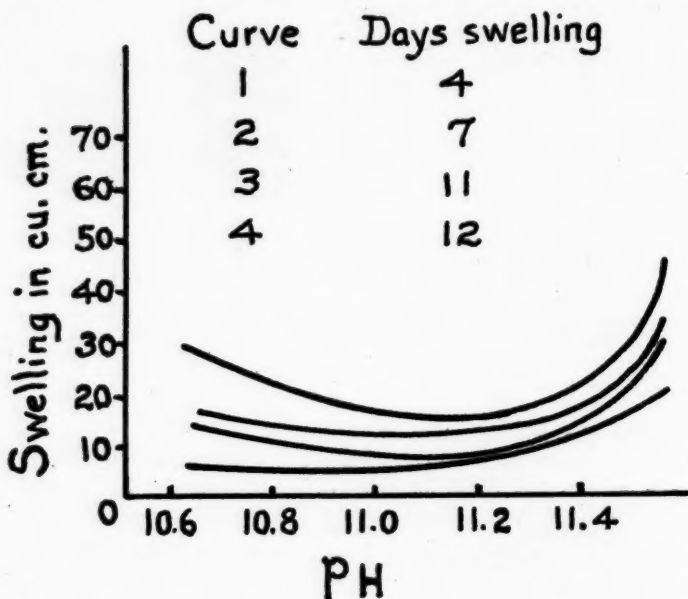


Figure 4

longer time an accumulation of water droplets was observed in the upper benzene layer.

Fig. 5 shows however another interesting phenomenon. The concentration of the rubber phase in latex is here only $1/10$ of that in the experiments described previously. The p_H of the latex in both experiments corresponds to Experiments 11 and 13. Table III gives these comparative values.

TABLE III

Experiment No.	Expt. 11	Expt. 14	Expt. 13	Expt. 15
Rubber content, g./l.	53.4	5.01	51.1	5.09
Ammonia content, mol./l.	0.76	0.70	0.016	0.0016
p_H	11.6	11.5	10.7	10.2

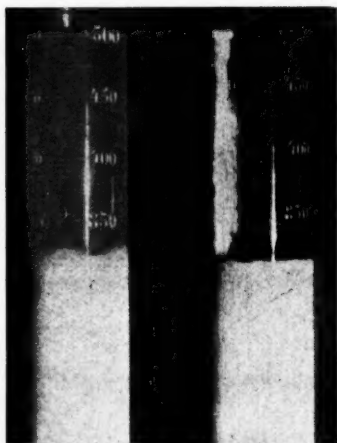
Though the p_H values of the corresponding experiments are the same within the limits of experimental error and the concentrations of the rubber mixtures are 10:1, the concentration of the ammonia changes to a greater degree. While it is the same with a high ammonia content, in weaker latexes the ratio is like the ratio of the rubber phases, viz., 10:1.

In regard to swelling, the two experiments are different. In Experiment 14, which corresponds to 11, swelling was at first at almost the same speed as in Ex-

periment 11. Experiment 15 shows, on the other hand, in general no more swelling, but only a creaming. In the illustration, the swelling in Experiment 14 is readily seen, but the creaming in Experiment 15 can unfortunately be seen only faintly.

Both Experiments 14 and 15 were observed for a longer period, and after ten days Experiment 14 showed no further increase in swelling, whereas Experiment 15 showed after only five days no further change in the cream layer. Nevertheless there was still present in the latex a sufficiently dispersed rubber phase so that outwardly no change in the color of the latex could be established. A microscopical preparation of both latexes showed either an essential decrease of small particles or a diminution of the Brownian movement. Figures 6 and 7 give only a poor representation of this appearance. However, by closer examination it can be observed that in latex of high ammonia content (Experiment 14) the small particles are all round and relatively small. On the other hand, in latex of low ammonia content (Experiment 15) a honeycombed structure can be plainly seen. This structure, which can only be seen by direct observation, results from a number of highly swollen latex particles.

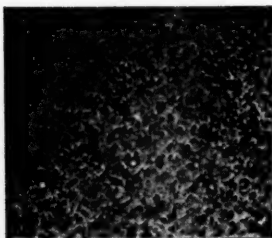
The diameter of these droplets, as can be estimated from the picture, is between two and three times as large as the diameter of the small and unchanged latex particles which are clearly shown. Furthermore, the shape of the swollen particles is angular and irregular.



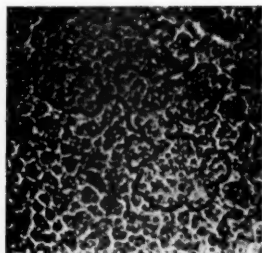
Expt. 14

Figure 5

Expt. 15



Expt. 14



Expt. 15

Magnification, 250 fold

Figures 6 and 7

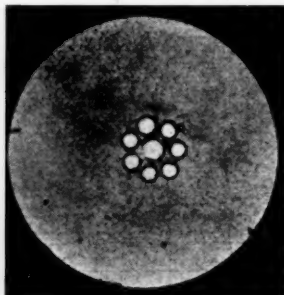
The impression is gained that high concentrations of ammonia protect the latex particle, because to a certain degree a layer impenetrable to benzene is produced in every individual particle. If this protection is lacking in media of low ammonia content, then the benzene would be diffused into the individual particles and would gradually bring about swelling. This observation is, however, directly contrary to the experiments on swelling previously described.

According to my opinion, distinction must be made between the swelling of the individual latex particles and the swelling of the coherent layer of formerly individual latex particles. If it is recalled that absorption phenomena on the boundary surface of a two-phase system have already been frequently observed, a swelling of latex should take place only to such an extent that there is an accumulation of latex particles in the boundary layer, with subsequent coagulation. We are concerned therefore with two different swelling phenomena, namely, with the swelling of the individual particle in the latex of weak ammonia content and with the formation of a coherent layer of latex particles and their subsequent swelling in an ammonia-rich latex.

I next tried to observe microscopically the formation of absorption layers at the boundary surface, for only by observing the latex during an experiment can one recognize the whole course of the individual phenomena. With ordinary microscopic methods, preparations can be made with which only the final condition can be studied. It was necessary therefore to make use of the micromanipulator of Péterfi. T. Péterfi has extensively described the use of the micromanipulator in the "Handbuch der Biologischen Arbeitsmethoden," Abt. V, Teil 2, S. 479 by



Shadow of glass needle
Magnification 34 fold



Magnification 25 fold

Figures 8 and 9

Abderhalden. In addition, E. A. Hauser has pictures and the method of using this apparatus in his book on latex.

In the following experiments I used in some cases a latex, the serum of which had been repeatedly filtered through a Bechhold filter. The remaining latex concentrate was each time dispersed again with strong ammonia. In spite of the removal of the original serum, this latex has remained unchanged for a year (filtered latex). In addition, I used a latex preserved in the ordinary way with ammonia (common latex). In most experiments, a dispersion diluted in the proportion of 1:10 up to 1:100 in water was prepared.

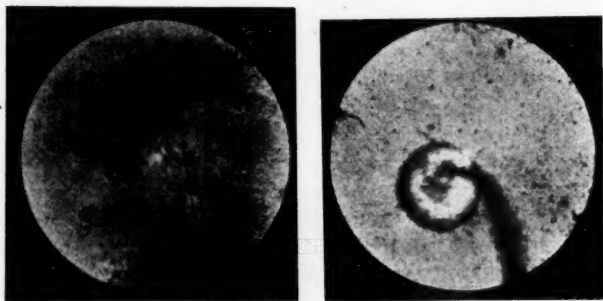
A drop of the filtered latex was introduced into the humidity chamber of the manipulator, fastened to the under side of the cover glass and mixed with a drop of a concentrated solution of Opalblau. Observations were made throughout with low power objectives (Zeiss-Objectives A or B) and strong oculars (Zeiss K 15); the microphotographs were taken with the Phoku (photographic ocular by Zeiss) with which Ortho-Isodux plates or panchromatic Agfa plates were used. A spot lamp with a weak converging light served as illumination.

Beside the colored drops of latex, there was then introduced a drop of xylene by means of pipette. The surface of contact was indistinctly seen and in the

boundary layer only a small accumulation of latex particles was to be seen. For some distance from the boundary layer (about $100\text{--}200\mu$) after a short time (about 5–6 minutes) long strings of pearl-like structures were formed which were connected but showed a feeble Brownian movement. Figure 8 shows such a string of pearls. After longer action by the xylene, about $\frac{3}{4}$ hour, the Brownian movement of the individual particles could be brought to a standstill, without further coagulation, flocculation, or swelling setting in.

It was so difficult to distinguish the colorless xylene from the highly colored prepared latex that observance of the separate phenomena of reaction was not possible. Moreover the rapid evaporation of the xylene made itself visible in an unpleasant way by the violent currents in the preparation, in spite of the fact that the humidity chamber contained a mixture of water-xylene. If it were possible to introduce drops of xylene into the latex, a closer observation might be possible.

To this end, I prepared a pipette with a small opening of about 20μ and with it a few drops of toluene were injected into a preparation of the same composition as above. After a little practice it was possible to introduce eight drops of toluene



Magnification 25 fold

Shadow of pipette

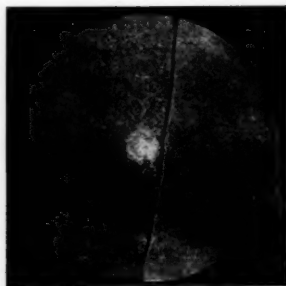
Figures 10 and 11

into the latex and at the same time follow the process visibly. As soon as the drops had reached the cover glass and adhered to it to some extent, they remained motionless, and other drops which could not be directed there burst and disappeared. Figure 9 shows the disposition of the drops of toluene three minutes after the injection. Their diameter varied between 80 and 120μ . Immediately after the injection, the drops were spherical, but after only 5 minutes the circular contour changed to an irregular shape. Simultaneously there appeared on the periphery radial streaks. This phenomenon is clearly shown in Fig. 9. In the course of the next few minutes the globules became coated with a wrinkled membrane and they shrank together.

The globules could not be punctured by a fine glass needle. Only when after ten minutes, as shown in Fig. 10, they were shriveled to a marked degree was it possible to tear the particles with a glass needle. I have selected the largest globule from the middle of Fig. 9; the other globules lie at various distances around the middle globule which has been cut into two parts. The contraction proceeded until after half an hour only a wrinkled membrane was left of the globule. In the boundary layer between both liquids there was also an adsorption of a substance in the form of a membrane. Toluene could diffuse through this, while

conversely no water apparently passed into the micelle. The latex particles in the vicinity were not further destroyed by the drops of toluene.

By a suitable arrangement it was possible to bring about an aggregation of latex particles in the boundary layer between the toluene and the serum, as shown in Fig. 11. A large drop of toluene was injected into a drop of ammonia-rich uncolored ordinary latex by means of a heated pipette. The diameter of the drop was about 460μ . The entire experiment was very difficult, because even after



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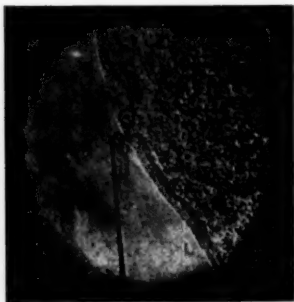


Magnification 25 fold

Figures 12 and 13

20 seconds the drop had disappeared from the field of vision. In spite of this, it was possible to confine the picture to one plate. It showed very plainly that there was an impoverishment of latex particles in the immediate vicinity of the drop of toluene and a distinct increase of the particles in the boundary layer. In individual places, a migration of particles from the drop could be observed as, for example, under the bent shadow of the pipette. The more distant surroundings of the drop remained unaffected by the adsorption phenomena. The surface

energy of a boundary layer of benzene-water was relatively small, being only 52 ergs per sq. cm., whereas the energy of an aqueous serum layer against air is 117 ergs per sq. cm., *i. e.*, two to three times greater. It was to be expected that a latex-air surface of contact would show a still greater adsorptive power of latex particles. Figure 12 shows the correctness of this idea. It is a drop of ordinary latex which in the previous experiment adhered to the cover glass of the humidity chamber. On the right side of the photograph is the drop of latex with the zone of few latex particles which lies next to the adsorption boundary layer. On the left side the drop is in contact with the air. The boundary layer phenomenon is plainly seen after one



Magnification 25 fold

Figure 14

minute. Figure 13 shows another location of the same preparation. With a fine glass needle one part of the absorbed and coagulated boundary layer has been pushed apart. Liquid is flowing to the left from the drop, and on the new boundary surface latex particles can be seen still floating freely, but already on the point of adhering, which actually took place two minutes after the exposure.

Behind the aggregation of latex particles can be seen the space that is free of latex particles. That this phenomenon is not limited to this one latex is shown by Fig. 14, with a drop of a diluted (1:100) ammonia-rich latex which had creamed strongly. In spite of the fact that here are highly aggregated particles, the boundary layer is again clearly defined. From the puncture in the vicinity of the glass needle new latex already is flowing out.

The experiments described above show that the ammonia content of the latex determines its behavior toward solvents. It also explains why neither C. Harries nor Hinrichsen and Kindscher had such difficulties as I encountered. In both cases ammonia-free latexes were used. It is very probable that the latexes had been so diluted before they were shaken with the solvent that they were incapable of forming a boundary layer capable of swelling.

The foregoing experiments do however indicate that under some circumstances it is of advantage to use latexes of high ammonia content. If it is desired to impregnate fabric or similar material with latex, it is best to use latex with a high ammonia content, since such a latex can form a thick boundary layer. This will then adhere firmly to all solid boundary surfaces, with the result that a better impregnation is obtained than that obtained by evaporation. It is very likely that in these cases a large part of the serum can be expressed out again without removing too many rubber particles at the same time.

Summary

The swelling phenomena of latex in organic liquids such as benzene, toluene, or xylene were studied. As factors in the swelling power the following were observed: (1) the ammonia content of the latex; (2) the formation of a boundary layer in the surface of contact of both liquids.

Ammonia-rich latex on contact with aromatic hydrocarbons forms a boundary layer which in turn swells, with a great increase in volume.

Latex poor in ammonia forms no boundary layer and therefore does not swell. On the other hand, the hydrocarbon may diffuse into the latex without disturbing the Brownian movement. Subsequently the diffused hydrocarbon is able to bring about the swelling of the individual latex particles.

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Aging of Rubber and Its Retardation by the Sur- face Application of Antioxygens¹

Diffusion Process

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THE deterioration of rubber may be due to any one or a combination of a large number of factors, such as oxidation, depolymerization, continued vulcanization, action of heat or light, and so on. The present paper will deal with the preservative action of antioxygens (12, 15) when applied on the surface of articles, and with some general remarks on the use of antioxygens.

Comparison of Accelerated Aging Tests

The only test not open to criticism is one which measures the aging of an article under actual service conditions and the writers used it in many control experiments. This test has the disadvantage of consuming an excessive amount of time and of not being suitable for a series of studies. Hence the necessity for artificially hastening the deterioration of the rubber articles. This accelerated aging is obtained, as is well known, by the use of such agents as heat, light, or compressed oxygen used separately or simultaneously. There is some doubt as to which accelerated aging test gives results most similar to natural aging.

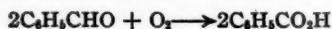
OXYGEN AGING—The test using compressed oxygen, either hot or cold, has aroused considerable interest in the last few years. The harmful action of oxygen on rubber was recognized as early as the middle of last century (1, 3, 4, 7, 9, 10, 11, 18, 21, 22). In an earlier series of the publications (15) the writers have shown that the changes caused by oxygen in organic substances are of two distinct kinds: one is of an ordinary chemical nature, the other, catalytic.

The first type may be represented by a stoichiometrical equation where the quantity of matter altered is proportional to the mass of oxygen that reacts. A typical example of this kind of reaction is the oxidation of benzaldehyde to benzoic acid. The extent of the reaction may be measured by the

¹ Received August 5, 1929.

² Deceased.

quantity of oxygen which reacts according to the following equation:



The second kind of change due to oxygen, to which the writers have frequently called attention since starting their work on autoxidation, is not due entirely to the oxidation reaction. It is some secondary transformation, such as a polymerization, in which the quantity of material transformed bears no stoichiometric relation to the quantity of oxygen causing such transformation. A typical example of this is the transformation of acrolein into an insoluble resin (disacryl). This change is produced by the merest trace of oxygen (13, 16), a mass 0.00001 as great as the aldehyde being sufficient. The writers have attributed this type of reaction to the catalytic action of peroxides formed by autoxidation. This type of change is most serious because it requires such minute quantities of oxygen for its initiation.

In practice with styrene, drying oils, rubber, etc., these two kinds of change occur simultaneously, their relative effects being dependent upon the conditions under which the test is carried out. The resultant effect will therefore be variable for the same quantities of oxygen absorbed by identical substances.

It is therefore not necessary merely to speed up the absorption of oxygen by rubber to accelerate natural aging. If in a given experiment the loss of elastic properties is due to change catalyzed by oxygen (20), it is useless or even harmful, according to the information desired, to facilitate the oxidizing action too greatly. An excess of oxygen may even lead to a false conclusion by completely changing the course of the reaction. Thus acrolein, which is completely transformed into disacryl by the catalytic action of minute traces of oxygen, no longer produces disacryl in the presence of an excess (15). Compressed oxygen should therefore not be used in the study of the accelerated polymerization of acrolein.

The oxygen test, in spite of its present popularity, may not always lead to proper conclusions in a study of the deterioration of rubber.

HEAT AGING—Deterioration due to heat must not be considered as giving a faithful picture of natural aging, even when carried out according to the improved technical method described by Geer (5). The test, however, does give certain important information relative to changes that will occur at ordinary temperature. In addition it can be used to predict the behavior of rubber materials that are designed to operate at elevated temperatures.

The writers have used the resistance to heat as an empirical test having no essential relation to the normal changes that might occur at lower temperatures. Samples are heated in a hot-air oven at 90° C. until the control samples show considerable deterioration, which is about 100 hours. Different lots are placed in separate containers to avoid contamina-

tion of the samples, especially the controls, by vapors or dust of antioxygens which might be evolved from other samples. It is not considered necessary to pass a current of air through the oven, since rubber does not oxidize rapidly enough to decrease noticeably the oxygen content of the air in the oven where spontaneous circulation and renewal are relatively rapid. The use of controls minimizes errors due to differences between successive experiments.

LIGHT AGING—Exposure to ultra-violet light should not be considered a practical test (2) except where objects are to be used under similar conditions. As a matter of fact, irradiation with ultra-violet light introduces an additional deteriorating factor, ozone, which does not exist under the ordinary conditions of use. Deterioration due to ozone is an entirely different phenomenon than that due to oxygen and is not subject to the same influences. Those materials giving protection against ozone will, in general, not be the same as those which afford protection against oxygen. By special experiments the writers have established that "antioxygens" are not "antiozones." Ozone itself should be avoided in tests where it is desired to determine experimentally the efficiency of an antioxygen in rubber. The writers made several tests by sunlight.

Preservation of Rubber by Diffusion Process of Antioxygens

The preservation of rubber (12) by the use of materials having antioxygenic properties may be carried out by various methods.

One process, outstanding for its simplicity and efficiency, consists in depositing the antioxygen on the surface of the rubber and is therefore applicable to the treatment of finished objects.

The efficiency of this process of protecting rubber might, as a matter of fact, be advanced as an argument in favor of the "varnish theory" (17), which attributes to the antioxygen a mechanical role consisting simply in preventing the contact of oxygen with the object that is liable to be oxidized. In this process the method of using the antioxygen is similar to the application of a varnish. However, it is shown here that the antioxygen penetrates into the article by diffusion. It does not, therefore, form an isolating film at the surface, and this mode of protection by surface application cannot be invoked in favor of the varnish theory.

ARTICLES TESTED—Experiments have been carried out on manufactured commercial articles such as rubber sheeting, stoppers, tubes, air containers, bathing caps, erasers, fountain-pen tubes, etc. Since the properties of rubber sheeting can be more conveniently measured in a quantitative manner, this material has been used for the majority of tests.

METHODS OF APPLYING ANTIOXYGEN—(1) The antioxygen may be spread directly on the surface of the rubber without the use of any diluent. This process suffers from the disad-

vantage that it uses too much of the active material and the application may not be uniform.

(2) The article may be exposed to the vapors of the antioxygen at a temperature depending on the vapor pressure of the antioxygen. This process may be convenient in special cases.

(3) The most convenient method of application consists in applying the antioxygen in a dilute condition—that is, mixed with inert powder or a liquid to give a true solution, emulsion, or suspension. The best results have been obtained with the antioxygen in true solution.

ANTIOXYGENS USED—The experiments carried out with three phenols—hydroquinone, catechol, and guaiacol—are described to demonstrate the application of the method. Phenols were chosen as being the simplest type of compound with which to study the phenomenon.

Note—The antioxygen action of phenols on rubber has been the subject of many papers (8, 19, 1, 23, 6) since the granting of the patent to the writers (12). Furthermore several antioxygens have come into extensive commercial use.

PROCEDURE—The efficiency of the treatments was compared by determining the ultimate tensile strengths of three series of samples. The first two served as controls, one remaining unaged, and the other being aged along with the third sample which had been treated with the antioxygen. In order to determine the influence of the solvent used in the treatment, the writers have measured, on different occasions, the ultimate tensile strength of a fourth series of samples which were aged along with the others after first being impregnated by the solvent. The figures given in Table I represent the ultimate tensile strength as determined by breaking a series of six samples given the same treatment. The rubber sheeting was painted with the solution of the phenol and then allowed to dry for 24 hours.

Many other experiments not recorded here were also made. In many of these tests too strong a solution was used, for the phenol remained for the greater part on the surface and when it crystallized was largely lost during the further manipulations. In practice it would be better to use more dilute solutions even though it were necessary to make several applications.

RESULTS—It is possible to show the efficiency of this method of preserving rubber in a very striking manner. Half of the surface of a small sample of sheet rubber may be protected by painting one end or by dipping the lower half in a solution of the antioxygen. If the sample is now subjected to the aging test (heat, light, or natural), it will be observed that the treated end retains its elasticity whereas the other becomes short and brittle. In order that this experiment may be completely successful, it is necessary that one portion of the surface remain free from all trace of contamination by the antioxygen. It is even preferable to

protect the untouched portion against the vapors of the anti-oxygen during the aging test, especially when an oven is being used.

The nature of the solvent used to apply the antioxygen is of importance, as is shown in Table I, although it is difficult to give a rule of general application. Slight influences may profoundly modify the activity of the antioxygen or even completely reverse its action. However, ether seems to be the best solvent for use with the phenols that were tried, whereas turpentine appears to have a detrimental effect. For other antioxygens it may be that the best solvent will not be ether. In any case, no single solvent or mixture of solvents should be adopted for use except after careful study.

Table I—Effect of Heat on Protection of Rubber by Antioxygens

ANTIOXYGEN	SOLVENT	ULTIMATE TENSILE STRENGTH PER STANDARD CROSS-SECTIONAL AREA ^b		
		Control, not heated	AFTER HEATING FOR APPROX. 100 HRS. AT 90° C.	
			Not treated	Treated with phenol
		Grams	Grams	Grams
Hydroquinone	Ethyl ether ^a	5700	2700	5080 ^c
Hydroquinone	Ethyl ether ^a	6266	874	2125
Catechol	Ethyl ether ^a	5700	1676	2633
Guaiacol	Ethyl ether ^a	5700	1676	5390
Hydroquinone	Distilled water	6266	874	700
Catechol + guaiacol	Distilled water	3655	1687	780
Hydroquinone	Methanol (99%)	6266	874	1050
Hydroquinone	Methanol (83%)	5433	2300	976
Hydroquinone	Methanol (52%)	5433	2300	5180
Hydroquinone	Ethyl alcohol (95%)	6266	874	2373
Hydroquinone	Ethyl alcohol (67%)	6266	304	1620
Hydroquinone	Benzene	5700	1550	<1550
Hydroquinone	Acetone	5700	1550	1000
Hydroquinone	Turpeneol	3655	508	1774
Guaiacol	Turpeneol	6266	874	< 300
Coal-tar creosote	Methanol (99%)	5433	1665	3686
Hydroquinone	Benzene 10, turpeneol 1	5700	2970	4320
Hydroquinone	Benzene 5, ether 5	5700	1676	2993
Hydroquinone	Benzene 4, acetone 5	5700	1550	<1550
Hydroquinone	Acetone 8, turpentine 3	5700	1550	1880
Hydroquinone	Ether 10, turpeneol 1	5700	2700	5730
Hydroquinone	Ether 10, amyl ether 1	5700	1676	6560
Guaiacol	Ether 10, turpentine 1	5700	4020	< 700
Guaiacol	Benzene 10, turpentine 1	5700	4020	< 700
Hydroquinone	Ether, ^a applied to one side	6260	870	2830
Hydroquinone	Ether, ^a applied to both sides	6260	870	2120

^a 10 per cent solution.

^b Cross-sectional area not recorded.

^c The numbers in italics point out that the diffusion process may give a remarkable preservation.

It is highly probable that all of the antioxygen did not remain deposited on the surface of the rubber, but that it penetrated into the sample either when the sample was swollen by the solvent or by progressive diffusion after drying. Hence the name "diffusion process" is proposed for this method of protecting rubber.

The sample treated on one side only was as thoroughly protected as the sheet treated on both sides, proving that the antioxygen entered and thoroughly penetrated the sample.

A commercial eraser, which hardens superficially in a few days, was treated in a similar manner with an ether solution of hydroquinone. After it had dried for several weeks the surfaces were cut away, thus removing the superficial layer of antioxygen. The interior thus bared was perfectly protected and did not show any change for more than a year. The antioxygen had thus penetrated by diffusion into the interior of the material.

NATURAL AGING TESTS—Natural aging tests, in which the objects were treated by the diffusion process and subjected to normal use in the dark or in the sunlight, were started at the beginning of the writers' investigation long before their first publication (12). These tests have frequently been repeated either by the writers or by their assistants. The results obtained were often remarkable and establish with certainty the value of the diffusion process.

Advantages of Diffusion Process

PROTECTION IS ASSURED—In all applications where it is necessary to rely upon an efficient protection of rubber—as in surgeons' gloves, gas masks, aeronautics, etc.—the process offers security to the user because it assures the protection of his rubber articles.

PROTECTION MAY BE RENEWED—The antioxygen deteriorates in use. This phenomenon has already been described (14). The speed of the deterioration of the catalyst varies according to conditions, but will increase in proportion to the work it is called upon to do—that is to say, in proportion to the resistance which it must offer to a more energetic action of oxygen (highly concentrated oxygen, action of heat or light). Thus the protection given to the rubber does not last indefinitely and it may be worth while, especially for objects exposed to heat and light, to prolong the protection by a second application of antioxygen. The process by diffusion lends itself to renewal of the protection. It alone provides a means of retarding deterioration after it has once begun.

PROTECTION IS RATIONAL—The oxidation of the interior of rubber articles by oxygen which diffuses is not negligible. However, most of the oxidation occurs on the surface. As a matter of fact, in the vicinity of the atmosphere the oxygen will be most highly concentrated and it is in these regions that the deteriorating action of light will occur. It is therefore in the interests of efficiency to have a higher concentration of antioxygen on the surface. The diffusion process fulfils this condition and thus appears to be a rational way of applying antioxygens to rubber.

Remark on Use of Antioxygens

In order to avoid disappointment, one must take advantage of the general information that has been acquired regarding the peculiarities of antioxygenic catalysis. It is most important to keep always in mind the important

fact of inversion of antioxygen action—that is, the hastening of the autoxidation and the changes that result. As the writers have frequently stated (15), a given substance should not be given as an antioxygen (or pro-oxygen) but, in a more general way, as a catalyst of autoxidation, without being precise as to the sign of the catalytic action. The sign (positive or negative) of the catalysis depends as much on the experimental conditions as on the nature of the catalyst. The experiments given above furnish new examples of this inversion of the antioxygen action of a catalyst.

There is a danger, therefore, if one does not take all the necessary precautions, of hastening the loss of the rubber objects in trying to protect them.

"Antioxygens" vs. "Antioxidants"

Since 1921 the writers have frequently called attention to the property, possessed by numerous materials, of preventing the action of free oxygen on a wide range of autoxidizable substances. They have proposed the name of "antioxygens" for these materials. This term has been adopted by many workers who publish articles dealing with antioxygenic phenomena. However, certain writers use the word "antioxidant." The writers believe that this substitution is contrary to scientific usage and should be avoided.

"Antioxidant" means that which opposes oxidation. It might therefore be thought to hinder the action of such reagents as potassium permanganate, chromic acid, nitric acid, hydrogen peroxide, ozone, etc. Considered in this sense "antioxygens" are not antioxidants. Many of them are even destroyed by oxidizing agents. In order to use "antioxygens" they must be preserved from contact with oxidizing agents.

Some errors in thought which may arise from the use of the term "antioxidant" are shown by the following examples:

The action of oxygen on autoxidizable substances gives as preliminary products peroxides, which are true oxidizing agents. "Antioxygens" are not "antioxidants," as has just been shown, but are in general unable to resist oxidizing agents and may therefore be destroyed by the peroxides. Thus an article which is to be protected against oxygen, after having been subjected to the action of the air, will need a greater proportion of an "antioxygen" to make up for that which will be destroyed by the peroxides already formed. With the term "antioxidant" there is the risk that this peculiarity will be forgotten and give rise to disappointing results.

In the rubber industry certain workers have used exposure to ultra-violet light as a test of the efficiency of protection against oxygen. The deterioration caused by ultra-violet light is probably due to the action of ozone. Now, "antioxygens" generally are not "antiozones," but are often destroyed by ozone. It is thus a mistake to test the efficiency of antioxygens under conditions where ozone may be present. Free oxygen is the only suitable material for testing, and not any oxidizing agent chosen at random, as has been believed by certain workers, deceived by the word "antioxidant."

The term "antioxygen," precise and restricted, allows of no ambiguity.

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Studies of the Aging of Vulcanized Rubber

X.—The Relation between Degrees of Oxidation of Vulcanized Rubber and the Occurrence of the Maximum State of Acetone Extracts

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One of the authors (Yamazaki) noticed in his fourth report on studies of the aging of vulcanized rubber (*J. Soc. Chem. Ind. (Japan)*, 30, 812 (1927)) that the acetone extract of some of the aged vulcanized rubber decreased after having increased to the maximum point according to the conditions of aging in relation to degrees of vulcanization. The author, therefore, inferred the cause to be the partial formation of some acetone-insoluble products when the oxidation of vulcanized rubber had proceeded considerably. Since there was no quantitative proof, the authors experimented to prove this point for both the samples consisting only of rubber and sulfur and samples containing accelerator and zinc oxide. In addition to this, a parallel test was made with the non-extracted vulcanized rubber samples to prove the validity of the acetone extraction.

Experiment I—The Relation between the Oxidation of the Acetone-Extracted Vulcanized Rubber Samples and the Maximum State of Acetone Extracts

(1) *The Samples Used and the Procedure.*—The samples were the same as in the ninth report, with the following composition:

Stock A—Rubber 92.5%, S 7.5%.

Stock B—Rubber 90%, S 3.5%, ZnO 5.6%, D. P. G. 0.9%.

The curing periods of the samples used for this experiment were 100 and 180 min. for stock A and 20, 40, 60, and 80 min. for stock B at a steam pressure of 42 lbs. per sq. inch. After the vulcanized rubbers were finely divided, they were extracted with acetone and dried *in vacuo* and used for the following experiments as the original samples.

These extracted samples were aged at 70° C. for stock A and at 70° C. and 90° C. for stock B. After heating for definite intervals, the weight increase and the acetone extract were measured.

(2) *The Results of the Experiment.*—(a) *Aging of the Samples Using Stock A at 70° C.*

TABLE I
THE RELATION BETWEEN THE WEIGHT INCREASE AND THE ACETONE EXTRACTS BY OXIDATION OF STOCK A

Time of Heating, Hours	100 Min. Vulcanizate			180 Min. Vulcanizate		
	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.
50	0.54	1.34	0.05	1.76	10.41	0.31
100	1.43	8.14	0.14	4.01	20.27	0.55
200	4.70	25.75	0.36	9.90	29.11	0.68
300	8.00	26.75	0.39	11.80	32.10	0.76
500	12.55	22.71	0.37	14.17	20.43	0.52
1000	15.54	24.10	0.38	15.47	20.83	0.54

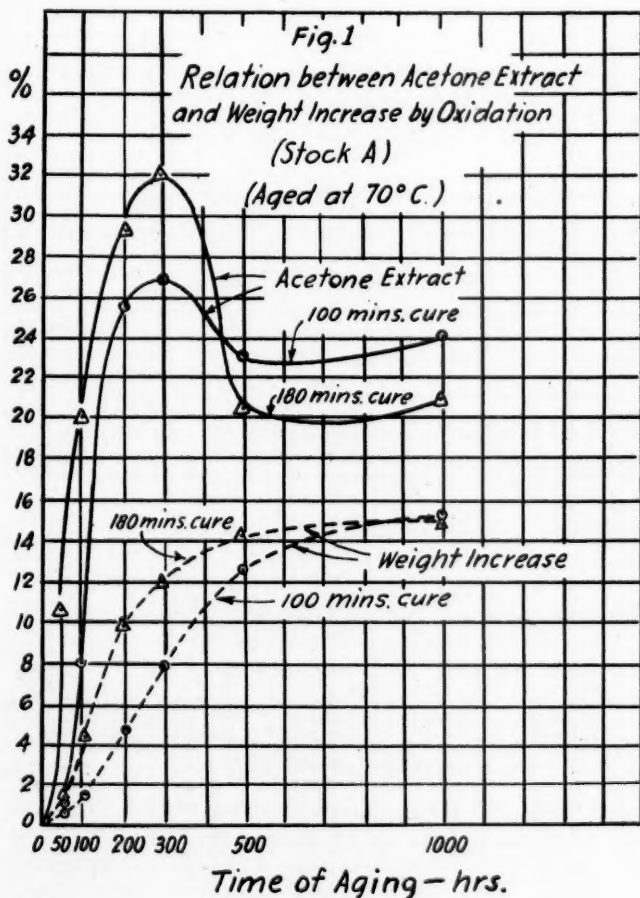
(b) *Aging of the Samples Using Stock B at 70° C.*

TABLE II

THE RELATION BETWEEN THE WEIGHT INCREASE AND THE ACETONE EXTRACTS BY OXIDATION OF STOCK B

Time of Heating, Hours	20 Min. Cure			40 Min. Cure		
	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.
100	0.26	0.61	0.03	0.60	1.73	0.04
250	0.65	3.80	0.06	1.20	5.10	0.08
500	1.35	10.56	0.10	2.14	14.55	0.15

Time of Heating, Hours	60 Min. Cure			80 Min. Cure		
	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.	Weight Increase, Per cent.	Acetone Extract, Per cent.	Sulfur in the Acetone Extract, Per cent.
100	0.99	3.14	0.06	1.56	5.11	0.08
250	2.01	8.40	0.15	2.60	13.50	0.20
500	3.33	22.47	0.25	3.77	26.45	0.33



In this case the maximum state of the acetone extract did not appear. But it seems to be reasonable to think that the cause lies in the incomplete oxidation or that it has not reached such a state where the acetone extract begins to decrease.

(c) *Aging of the Samples Using Stock B at 90° C.*

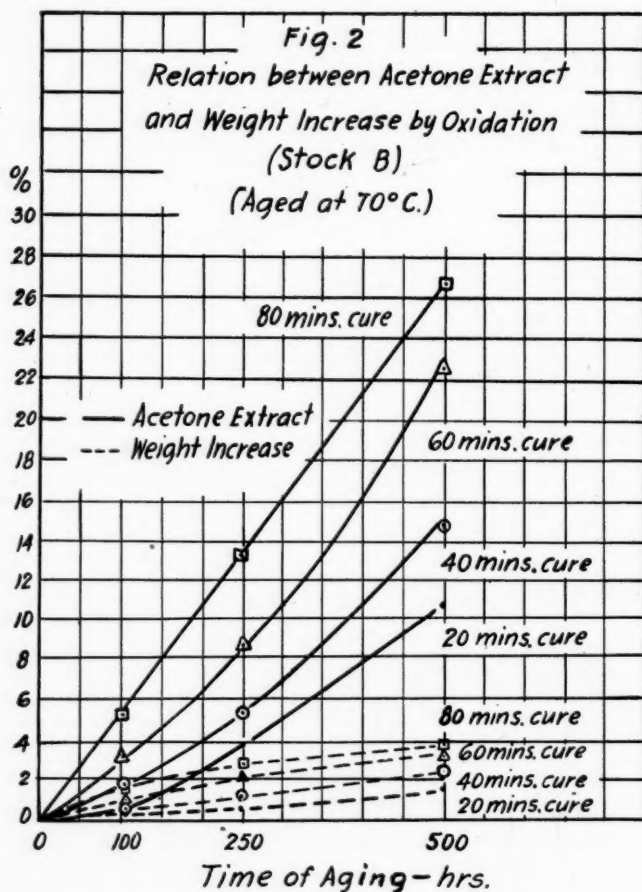


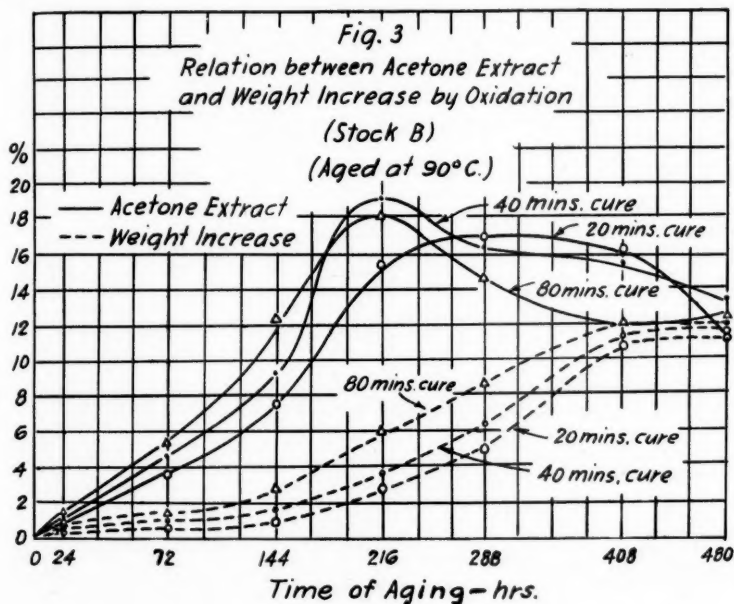
TABLE III

THE RELATION BETWEEN THE WEIGHT INCREASE AND THE ACETONE EXTRACTS BY OXIDATION OF STOCK B AT 90° C.

Time of Heating, Hours	20 Min. Cure		40 Min. Cure		80 Min. Cure	
	Weight Increase, Per cent.	Acetone Extract, Per cent.	Weight Increase, Per cent.	Acetone Extract, Per cent.	Weight Increase, Per cent.	Acetone Extract, Per cent.
24	0.20	0.85	0.40	1.05	0.83	1.56
72	0.46	3.44	0.75	4.43	1.21	5.23
144	0.70	7.41	1.55	9.09	2.97	13.15
216	2.60	15.45	3.20	19.00	5.80	18.02
288	5.20	16.90	6.10	16.23	8.75	14.48
408	11.24	16.21	11.45	15.57	11.80	11.82
480	11.50	11.63	11.75	13.41	11.87	12.31

In this case the maximum state of the acetone extracts definitely appeared. Therefore this state can occur not only in the rubber-sulfur mixture but also in the mixture containing accelerator and mineral filler.

(d) *The Elementary Analysis.*—To verify the authors' opinion more definitely elementary analysis was performed upon the aged vulcanized rubber samples



from which the acetone-soluble oxidation product was previously removed, believing that the amount of oxygen in such samples should be greater as oxidation proceeded. The results were as follows:

TABLE IV

ELEMENTARY ANALYSIS OF THE AGED VULCANIZED RUBBER FROM WHICH ACETONE-SOLUBLE OXIDATION PRODUCTS WERE REMOVED

	Samples of 100 Hrs. Aging	Samples of 300 Hrs. Aging	Samples of 500 Hrs. Aging
	Per cent.	Per cent.	Per cent.
C	74.22	71.65	68.20
H	11.63	11.30	11.20
S	4.05	3.88	3.46
Ash	1.30	1.20	1.44
O	8.80	11.97	15.70

The results were as expected.

Experiment II—The Weight Increase of Acetone- and Non-Acetone-Extracted Vulcanized Rubber by Heating

The authors used in the above experiment the samples which were previously extracted by acetone under the assumption that acetone treatment depends only on the speed of oxidation and not on the final product. The validity of the acetone extraction was definitely proved by this experiment.

(1) *The Samples Used and the Procedure.*—Two series of finely divided stock A samples were prepared for each curing time. The acetone extracted and non-extracted samples were heated at 70° C.

(2) *The Results of the Experiment.*—(a) *The Increase of Weight of the Non-Extracted Vulcanizate.*

TABLE V

THE INCREASE OF WEIGHT OF NON-ACETONE-EXTRACTED VULCANIZATE				
Time of Heating, Hours	100 Min. Cure, Per cent.	140 Min. Cure, Per cent.	180 Min. Cure, Per cent.	220 Min. Cure, Per cent.
50	-0.02	-0.03	0	0.98
100	0.04	0.20	1.43	3.24
150	0.82	0.96	2.89	5.00
250	3.51	3.98	7.13	8.66
350	4.44	5.16	8.80	9.78
500	5.39	6.54	10.10	10.68
700	7.29	8.86	11.10	11.34
1000	10.68	11.10	12.00	12.13

(b) *The Increase of Weight of the Acetone-Extracted Vulcanizate.*

TABLE VI

THE INCREASE OF WEIGHT OF THE ACETONE-EXTRACTED VULCANIZATE

Time of Heating, Hours	100 min. Cure, Per cent.	140 Min. Cure, Per cent.	180 Min. Cure, Per cent.	220 Min. Cure, Per cent.
24	0.36	0.77	1.24	2.60
72	1.60	3.39	4.25	7.61
144	5.04	6.23	7.76	9.61
240	8.61	9.40	10.36	10.80
360	11.21	11.34	12.05	11.68
480	12.43	12.34	12.68	12.43

The above results show that although there are considerable differences in the speed of oxidation between acetone-treated and non-treated samples, oxidation of the latter finally approaches to that of the former. Therefore it was permissible to use acetone-extracted samples in our experiments.

Summary of the Experiments

(1) Using the rubber-sulfur mixture and the mixture containing accelerator and zinc oxide, the relation between the maximum state of acetone extracts and the degree of oxidation was studied quantitatively.

(2) In carrying out the above experiment, the samples previously extracted were used in order to accelerate the oxidation and to eliminate the influence of the free sulfur and rubber resin, etc. The aging was conducted at 70° C. for the rubber-sulfur stock and 70° C. and 90° C. for the stock containing accelerator and mineral filler and the increase of weight and the amount of the acetone extract were measured at definite intervals. The maximum state occurred in both cases, but for the case containing accelerator and filler the occurrence was comparatively slow. The decrease of acetone extract after the maximum state was shown to be due to partial formation of some acetone-insoluble products in the aged vulcanized rubber when oxidation proceeds considerably.

(3) From the elementary analysis made on the aged samples from which acetone-soluble oxidation products were previously removed, it was shown that the oxygen content in these samples increased as aging proceeded.

(4) The validity of using the acetone-extracted samples was proved by comparing the speed of oxidation of the acetone-extracted and non-extracted samples.

(5) From the experimental results, the general validity of the occurrence of the maximum state of the acetone extracts and its industrial application was discussed.

Studies of Conditions Affecting the Vulcanization of Rubber

IV. Heat Reaction during Vulcanization

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The heat reaction during vulcanization was traced by means of a differential thermocouple, of which one contact point was placed in a sealed glass tube enclosed in the sample and the other in the heating medium of a small electric furnace, *e. g.*, asbestos yarn windings. Specially prepared rubber precipitated from latex by acetone was milled with varying quantities of sulfur and was vulcanized at 155° C. The heat change was observed during the vulcanization. The curves are shown in Fig. 1. Although the absolute or relative amount of heat evolved

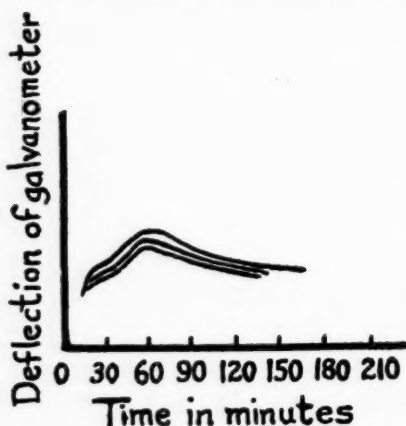


Figure 1

seems to be shown by the ordinate of the curves, it is not the case because of the uneven thermal resistivity of the samples. From these curves, therefore, it may only be seen that the profiles of them are similar to each other, showing maximum points at 60 to 70 minutes and decreasing asymptotically to a horizontal line, *i. e.*, the temperature of the heating medium of the furnace. It is observed that the maximum points lie at about the same period, though the sulfur contents of the samples were varied. Similar results are shown by Perks (*J. Soc. Chem. Ind.*, 1926, 142T). The present author analyzed the vulcanizates corresponding to the maximum points of the curves, the results of which are shown in the following table.

Sample	Rubber	Sulfur	Per cent. Free Sulfur	Per cent. Combined Sulfur	$\frac{\text{Free Sulfur} \times 100}{\text{Total Sulfur}}$
D	68	32	17.69	14.35	56
E	68	20	13.10	8.17	61.5
F	68	10	8.47	5.72	59.8

It is observed that the percentage of free sulfur to total sulfur is about 50-60% in samples contg. various quantities of sulfur.

In the next experiments, the temperature of vulcanization was changed and the times until the maxima occurred were observed, and the resulting vulcanizates were analyzed as above.

The results were as follows:

Sample	Compounding	Temp. of Vulcanization, ° C.	Time, Min.	Free Sulfur $\times 100$ Total Sulfur
1	D (R, 68 : S, 32)	166	35	49.7
2	D (R, 68 : S, 32)	170	20	47.8
3	E (R, 68 : S, 20)	170	20	46.6
4	F (R, 68 : S, 10)	170	20	39.1

The coefficients of vulcanization seem to increase very slightly, while the decrease of vulcanization time is quite distinct. The temperature coefficient of vulcanization time from the above experiments is about 2 for every 10 degrees C., a value common to every chemical reaction. And the percentages of free sulfur to total sulfur are about the same excepting Sample 4, lying closely near to 50%.

It is very interesting that the maximum heat evolution occurs at about the half-way point of sulfur combination in each case, instead of at the starting time of the reaction, which case is general in every chemical exothermic reaction, and yet the temperature coefficient of reaction is like those of ordinary chemical reactions. And further, the composition of the vulcanizates corresponding to the maximum of heat evolution is about the same, 40-60% of total sulfur being combined, while the temperature and time of cure are markedly varied.

If it is possible to assume the vulcanization to be a chemical reaction and the rate of cure is affected by the disaggregation of rubber micelles, the rate of sulfur combination may be shown by the following formula:

$$\frac{dx}{dt} = K(R - x)(S - x) \quad (1)$$

where R is the number of chemical units of rubber per unit volume of reaction system, S is the same of sulfur, x is the number of chemical units of the reaction system chemically combined during time t , and K is the velocity constant.

In this case, if the reaction is chemically normal, R is constant, but in the present case, it varies with the disaggregation of rubber micelles.

If $r = R - x$

$$(1) \text{ becomes } \frac{dx}{dt} = Kr(S - x)$$

$$\text{therefore } \int rdt = \frac{1}{K} \int \frac{dx}{(S - x)}$$

$$\text{and } \int rdt = -\log(S - x) - C$$

If $t = 0, 0 = -\log S - C, C = \log S$

$$\text{therefore } \int rdt = \frac{1}{K} \log \left(\frac{S}{S - x} \right) = \frac{1}{K} \log \left(\frac{\text{Total sulfur}}{\text{Free sulfur}} \right) \quad (2)$$

It may be seen that from the beginning of the reaction the rubber micelles disaggregate as the combination between rubber and sulfur proceeds, and at length there is no more disaggregation when the velocity of the combination becomes maximum according to Equation 1. As the heat evolution is proportional to the reaction velocity, Expression 2 may be conceived to contribute to raise the temperature of the sample, dependent only on the ratio of total to free sulfur and independent of the time. And this is coincident with the present experiments as shown above, the maximum points of the curves lying at about the same time and the ratio of sulfur at those points being about the same.

Evolution of Hydrogen Sulfide from Vulcanized Rubber

Edward Wolesensky

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Abstract

The rubber-sulfur compound in vulcanized rubber splits off hydrogen sulfide at all times and at all temperatures between 25° C. and the temperature of complete thermal decomposition. The rate of evolution of the gas depends upon the temperature, time, the proportion of combined sulfur, and possibly other factors. The reaction affords a new explanation of the formation of hydrogen sulfide during vulcanization, and possibly also, in part at least, of the excess of combined sulfur over that required by the formula C_5H_8S . It may also be another factor in aging, though, perhaps, only a minor one, and presents a new problem in the regeneration of rubber.

I. Introduction

In the course of some experiments on the devulcanization of rubber, evidence of the liberation of hydrogen sulfide from the heated rubber was obtained. Questions immediately arose as to the extent and the conditions under which hydrogen sulfide is liberated from vulcanized rubber at elevated temperatures, and the bearing of this reaction on the desulfurization and regeneration of rubber.

The scientific literature affords very little information on this subject. Furthermore, the testimony of different writers is very conflicting and, on the whole, unsatisfactory.

II. Survey of Past Work

Payen¹ long ago claimed that from the beginning of the reaction of sulfur with rubber, at 135° to 160° C., and during the entire time of its continuation a slow disengagement of hydrogen sulfide takes place. He concluded that the sulfur replaces some of the hydrogen in the rubber hydrocarbon. Burghardt,² Pahl,³ and Bell⁴ (who claimed that the escape of hydrogen sulfide during vulcanization was a matter of common knowledge among rubber manufacturers) likewise adopted the "substitution" theory of vulcanization, as did also Terry⁵ at first, though later⁶ he accepted the "addition" theory of Weber and others. Bysow⁷ claimed that at temperatures up to 150° C., and, therefore, in ordinary vulcanization, there is no chemical combination between rubber and sulfur, but when the mixture is heated to 160° C. the temperature rises quickly to 215° C., with evolution of hydrogen sulfide. In the latter case, however, according to Bysow, the product is no longer vulcanized rubber, but a hard, porous, and worthless mass. Weber,⁸ on the other

¹ *Compt. rend.*, **34**, 453 (1852).

² "Thorpe's Dictionary of Applied Chemistry," **2**, 312 (1889).

³ *Gummi-Ztg.*, **15**, 145 (1900).

⁴ *Ibid.*, **8**, No. 19, 3 (1894).

⁵ *J. Soc. Chem. Ind.*, **11**, 972 (1892).

⁶ "India Rubber and Its Manufacture," 1907, p. 84.

⁷ *Caoutchouc et Gutta-Percha*, **8**, 5291 (1911); *Gummi-Ztg.*, **26**, 49 (1911).

⁸ *Z. angew. Chem.*, **7**, 112, 142 (1894); *J. Soc. Chem. Ind.*, **13**, 12 (1894); *Gummi-Ztg.*, **15**, 280 (1901); *Ibid.*, **16**, 563 (1902); "The Chemistry of India Rubber," 1902, p. 86.

hand, claimed that when the purest rubber hydrocarbon is used it reacts with sulfur during vulcanization without disengaging even a trace of hydrogen sulfide, that the very small amounts of this gas which are evolved when ordinary commercial rubber is used are formed by the interaction of the "insoluble" component of rubber ($C_{30}H_{68}O_{10}$) with the sulfur, and that the reaction between rubber hydrocarbon and sulfur is an addition process. This view was also accepted by Schidrowitz,⁹ Perkin,¹⁰ Iterson,¹¹ Stevens,¹² and Bedford and Gray,¹³ as well as others.¹⁴ In this connection should be noted a rather surprising statement by Potts,¹⁵ who says, "Rubber has a molecule with two double bonds and the sulfur adds on with evolution of H_2S . Vulcanization is thus saturation." Is this a misstatement of Potts's views, or did he really know that hydrogen sulfide is split off from the rubber-sulfur compound? He gives no data to support the latter view.

In a recent paper Stevens and Stevens¹⁶ claim to have found combined sulfur in hard rubber considerably in excess of that required for the formula C_8H_8S ; they account for the excess by assuming replacement of hydrogen to a certain extent, with the formation of some hydrogen sulfide.

In all of the above-mentioned work the various investigators were interested in the formation of hydrogen sulfide only as a part of, or incidental to, the vulcanization process, and none of them appeared to consider the possibility of the splitting off of hydrogen sulfide from the rubber-sulfur compound after the latter is formed.

Burghardt¹⁷ observed that when vulcanized rubber is decomposed by the action of oils, the free sulfur is eliminated "probably as sulfuretted hydrogen," but he submitted no data to support this surmise.

Ahrens¹⁸ assumed the splitting off of hydrogen sulfide to account for a rather large decrease in both free and combined sulfur on aging, but he likewise gave no experimental evidence to support his assumption.

Dubosc¹⁹ observed a copious evolution of hydrogen sulfide when vulcanized rubber (from automobile tires) is subjected to destructive distillation. But he did not determine the amount of hydrogen sulfide formed; he merely assumed that all of the sulfur in the rubber is eliminated in this form. It is rather unusual for such decompositions to take place completely and quantitatively. Furthermore, it is quite obvious that owing to the particular design of his apparatus, the temperatures registered by his thermometer were entirely too low; for he states that the highest temperature reached in his experiment was $245^\circ C.$, at which point there was no further evolution of any gas and the rubber was completely carbonized, and, in fact, largely converted into coke, an hour and five minutes after heating was started. In the experience of the present writer, soft vulcanized rubber does not even begin to melt at $245^\circ C.$, much less to char; and after being heated at 285° to $289^\circ C.$ on a glycerine bath for 5 hours, although it is melted at this temperature it is still far from being completely carbonized; on the contrary, after cooling it still retains much of its rubbery character.

⁹ "Thorpe's Dictionary of Applied Chemistry," 4, 585 (1913).

¹⁰ *Chem. Eng. (Philadelphia)*, 18, 60 (1913).

¹¹ *India Rubber J.*, 56, 455 (1918).

¹² "Fourth Report on Colloid Chemistry and Its General and Industrial Applications, British Assoc. Advancement Sci.," 1922, p. 365.

¹³ *Ind. Eng. Chem.*, 15, 720 (1923).

¹⁴ Editorial Note, *Gummi-Ztg.*, 8, No. 19, 2 (1894).

¹⁵ *J. Soc. Chem. Ind.*, 32, 564 (1913).

¹⁶ *Ibid.*, 48, 55T (1929).

¹⁷ *Ibid.*, 2, 121 (1883).

¹⁸ *Gummi-Ztg.*, 28, 490 (1913).

¹⁹ *Caoutchouc et Gutta-Percha*, 15, 9617 (1918).

The above brief survey represents the state of our knowledge of the evolution of hydrogen sulfide from vulcanized rubber previous to the present work. The only one of the above-mentioned investigators who observed this reaction experimentally and apart from the vulcanization process was Dubosc, and he did little more than to identify the hydrogen sulfide qualitatively. It was believed that the reaction deserved closer study, and, accordingly, the present investigation was undertaken.

Since the completion of the work described in the following pages there has appeared a paper by Fry and Porritt²⁰ on the causes of the deterioration of hard rubber. This will be considered later in the present paper.

III. General Procedure

The general procedure was to heat the rubber sample in an appropriate vessel, such as a large test tube, a small Kjeldahl flask, or a special glass cylinder, through which was passed a stream of oxygen-free nitrogen, and pass the effluent gases through a solution of lead acetate acidified with acetic acid, or in some cases, when a qualitative test only was desired, into a tube containing a strip of filter paper moistened with lead acetate solution. The lead sulfide which was formed in the lead acetate solution was then rinsed out into a beaker, filtered off on a weighed Gooch crucible, washed, dried at 120° C., and weighed. In a number of cases the lead sulfide thus obtained was dissolved in strong nitric acid, the solution evaporated to dryness, heated with an excess of a solution of sodium carbonate, filtered, acidified slightly with hydrochloric acid, precipitated with barium chloride, and the barium sulfate thus obtained was weighed in the usual manner. Since the two sulfur determinations thus made always agreed very closely, the oxidation of the lead sulfide by nitric acid and its precipitation as barium sulfate was later omitted.

The source of nitrogen was a cylinder of the commercial gas. This was washed before passing it into the vessel containing the rubber sample by leading it through two absorption tubes each containing approximately 50 cc. of a nearly saturated solution of alkaline pyrogallol—10 g. of pyrogallous acid dissolved in 25 cc. H₂O and treated with 25 cc. of a 33 per cent. solution of sodium hydroxide—then through a tube containing concentrated sulfuric acid if dry nitrogen was desired, or through one or two tubes containing water if moist nitrogen was desired. Practically all of the oxygen in the nitrogen was absorbed in the first pyrogallate tube, the solution in the second tube remaining transparent and light brown in color for weeks at a time. As soon as the solution in this second tube became very dark and nearly opaque, fresh solutions were substituted in both tubes.

The absorption tubes were made of long pieces of glass tubing, about 10 mm. inside diameter, held in a nearly horizontal position with the ends turned up vertically for a length of about 12 to 15 cm. at each end. The nearly horizontal section of the tube was 90 to 95 cm. long, and at the entering end dipped sharply downward about 2 to 3 cm. below the main portion of the tube before turning upward. These tubes were usually placed at such an angle as to require about 30 seconds for the bubbles to traverse the entire length of the tube. Similar tubes were used for the absorption of the hydrogen sulfide, one such tube being generally sufficient to absorb this gas completely. When the hydrogen sulfide was evolved rapidly a second lead acetate tube was added merely as a check on the efficiency of the first tube, but only in one case was any precipitate formed in the second tube.

The various parts of the apparatus were joined together by means of rubber connectors, but the glass parts were pushed together as close as possible so as to

²⁰ *India Rubber J.*, **78**, 307 (1929).

leave a minimum of the rubber surface exposed to the gases within the apparatus. It is not believed that any appreciable errors in the results were introduced by this arrangement. When the decomposition chamber was empty, a stream of nitrogen could be passed through the apparatus for three days and nights without forming any appreciable amount of precipitate in the lead acetate solution.

The vessel containing the rubber sample was heated in a Freas oven for temperatures of 150° C. or less, in a glycerine bath for temperatures above 150° C. up to 290° C., and over a small free flame in the experiments on destructive distillation. The nitrogen was passed through the apparatus at the rate of about 20 to 25 bubbles per minute, and the flow of gas was continued overnight, after heating had been discontinued, to sweep out of the apparatus all of the hydrogen sulfide which had been disengaged during the heating.

IV. Experiments

Experiment 1.—A sample of soft vulcanized rubber, weighing 3.3953 g. and containing 3.71 per cent. of combined sulfur, 1.15 per cent. of free sulfur, and no fillers or pigments, was used. This was heated for 5 hours in a stream of undried oxygen-free nitrogen in a glycerine bath at a temperature of 285° to 289° C., the effluent gases being passed into a solution of lead acetate acidified with acetic acid. The temperature of the glycerine bath was raised to 285° C. in about one hour. The presence of hydrogen sulfide in the effluent gases was first noted at a bath temperature of 124° C., and was indicated by a light brown ring at the surface of the lead acetate solution. The rubber melted at 270° to 275° C. The lead sulfide formed in the lead acetate solution was filtered off on a Gooch crucible, washed, and dried. It weighed 0.1032 g., representing 0.0138 g. of sulfur, or 8.38 per cent. of the total sulfur in the original sample of rubber.

The lead sulfide, after being weighed, was converted into barium sulfate in the manner already described. The barium sulfate thus obtained weighed 0.1012 g. The calculated yield of barium sulfate from the lead sulfide used is 0.1007 g.

Experiment 2.—This experiment was very similar to the preceding, the chief difference being that the rubber was first extracted with acetone for 10 hours. By heating 4.9941 g. of the extracted rubber at 250° C. for one and one-half hours, 0.0348 g. of lead sulfide was obtained. This gives a rate of 4.6 mg. of lead sulfide per gram of rubber per hour. Another sample which had not been extracted, and which was heated at the same temperature for two hours, yielded 0.0770 g. of lead sulfide from 4.0834 g. of rubber, or at the rate of 9.4 mg. of lead sulfide per gram of rubber per hour.

Since the hydrogen sulfide is formed even in the absence of free sulfur it must come at least in part from the rubber-sulfur compound itself. The difference in the rates of evolution of the gas from extracted and unextracted rubber may be due in part to the interaction of free sulfur with some of the non-rubber components, as has been shown by the work of Bedford and Gray. It may arise also in part, as will be shown later, from the higher proportion of combined sulfur resulting from further vulcanization which undoubtedly took place.

At this point, however, the reader should be warned that a strict, quantitative comparison of the results herein described is not possible in most cases, since the experiments were not designed with that in view.

Experiment 3.—For this experiment the vulcanized rubber was extracted with a number of reagents for the purpose of removing the non-rubber components as far as possible. It was first extracted with acetone for 12 hours, then with chloroform for six hours, after which it was digested on the steam bath for four hours with a solution of 8 g. of potassium hydroxide in 175 cc. of alcohol, followed by digestion

for four hours with 200 cc. of a 10 per cent. solution of acetic acid in alcohol, and for four hours more with 200 cc. of a 10 per cent. aqueous solution of this acid. It was finally allowed to stand for about 16 hours in alcohol, after which it was dried in a vacuum at ordinary temperature and then once more extracted with acetone for four hours. The product after drying contained 3.35 per cent. of combined sulfur. A sample of the extracted material, weighing 6.3596 g., was heated in a stream of undried nitrogen as in the preceding experiments. The temperature was raised to 285° C. in about two hours, and then held at 285° to 290° C. for three and one-fourth hours. The lead sulfide obtained weighed 0.0792 g., representing 0.0106 g. of sulfur, or 4.97 per cent. of the sulfur present before heating was started. The lead sulfide here obtained was again converted into barium sulfate, and the latter weighed 0.0763 g. instead of the theoretical 0.0772 g.

On repeating the experiment with another sample of rubber similarly prepared, but heating it in dry nitrogen, similar results were obtained.

TABLE I
THERMAL DECOMPOSITION OF VULCANIZED RUBBER*

Temperatures, ° C.	Time of Heating, Hours	<i>In Dry Nitrogen</i>	Amounts of PbS Obtained
50	14	Slight ring at surface of lead acetate solution	
60	7	Slightly more	
80	7	Still more	
* Weight of sample, 18.5 g.		Combined S, 2.53 per cent.	
<i>In Moist Nitrogen</i>			
50	7	None	
90	7	Slight ring	
90	7	Stronger reaction	
70	7	Good test	
50	7	None	
50.....	7	Slight reaction with lead acetate paper	
<i>In Dry Nitrogen Again</i>			
120	12	0.0062 g. PbS	
140	15	0.0105 g. PbS	

Experiment 4.—In this experiment an attempt was made to remove the non-rubber components from the crude rubber before vulcanizing. One hundred and twenty-five grams of pale crepe were digested in an autoclave for seven hours at 200° C. with 800 cc. of a 2 per cent. solution of sodium hydroxide. This treatment was repeated with a fresh solution of the same composition. Then the rubber was similarly digested with two successive portions of 800 cc. of a 2 per cent. solution of sulfuric acid for two periods of seven hours each, followed by another digestion for seven hours with sodium hydroxide in the same manner as before. It was then digested for seven hours on the steam bath with a dilute solution of hydrochloric acid consisting of 2 volumes of water and 1 volume of concentrated HCl, then overnight with a dilute solution of ammonium hydroxide, then for 24 hours with alcohol, and finally dried in a vacuum oven at 100° C. The rubber was then mixed with 8 per cent. of sulfur and vulcanized for four hours in a vulcanizing press at 40 pounds steam pressure. The vulcanized rubber was crumbled on the compounding mill and digested for seven hours at room temperature in concentrated hydrochloric acid and overnight on the steam bath with dilute hydrochloric acid to remove iron introduced during milling. It was next digested on the steam bath for seven hours with water, then for 24 hours at room temperature with alcohol, dried in a vacuum oven at 100° C., and finally extracted with acetone for two days. It now contained 2.53 per cent. of combined sulfur and 0.03 per cent. of nitrogen, the latter being determined by Kjeldahl digestion and titration.

A sample of this rubber, weighing 18.5 g., was heated at various temperatures and for various periods of time as shown in Table I, with the results indicated.

The test for hydrogen sulfide appeared to be more difficult to obtain when moist nitrogen was used instead of the dry gas. For this the writer is unable to give a satisfactory explanation. However, similar results were obtained in other experiments under similar conditions. At any rate the evidence fails to show an increased evolution of hydrogen sulfide in the presence of moisture.

Experiment 5.—An attempt was made in this experiment to purify the rubber as much as possible in the latex form by means of the alkali-digestion method, essentially as recommended by Pummerer.²¹ Six hundred milliliters of ammonia-preserved latex were mixed with 600 cc. of an 8 per cent. solution of sodium hydroxide and 1 liter of water. The mixture was digested at about 50° C. for 48 hours, with frequent shaking during the day, in a stoppered flask from which the air had been displaced by nitrogen. At the end of the second day the flask was nearly filled with water and the rubber allowed to "cream" overnight. The lower layer (clear) was then siphoned off. This treatment was repeated three more times, but the digestion was continued for only 24 hours each time. The last time this was done the rubber failed to "cream" after several days, and 75 g. of sodium chloride were dissolved in the liquid, after which the rubber separated from the aqueous solution sharply within 24 hours. After siphoning off this last solution, the rubber was washed by filling the flask with water, shaking thoroughly, allowing it to cream, and siphoning off the clear solution. This cycle of operations was carried out about ten times, until the spontaneous coagulation of the rubber made further washing in this manner impracticable. As the washing proceeded it was found necessary to add increasing amounts of sodium chloride to induce separation of the rubber from the aqueous solution. At the end the aqueous solution, after being acidified with acetic acid and filtered to remove remaining particles of suspended rubber, still reduced an alkaline solution of permanganate, but did not give a distinct biuret reaction.

The rubber thus obtained was washed for a few minutes on the mill (corrugated rolls) and dried in a vacuum oven at 100° C. It was then mixed with 8 per cent. of sulfur and vulcanized in a press at 40 pounds steam pressure for 6.5 hours. About 35 g. of the product were crumbled on the mill and extracted for two days with acetone. The rubber then contained 7.37 per cent. of sulfur (combined) and 0.03 per cent. of nitrogen, the latter being determined by Kjeldahl digestion followed by a colorimetric estimation with Nessler's reagent.

A sample of this extracted product, weighing 27.6 g., was heated in a stream of dry nitrogen as shown in Table II with the results indicated.

TABLE II

THERMAL DECOMPOSITION OF VULCANIZED RUBBER*

Temperature, °C.	Time of Heating, Hours	Amount of PbS Obtained, Grams	Temperature, °C.	Time of Heating, Hours	Amount of PbS Obtained, Grams
25-30	7	None	140	18	0.0162
50	7	(**)	200	12	0.1019
100	18	0.0013	200	18	0.0369

* Weight of sample, 27.6 g. Combined S, 7.37 per cent.

** Slight ring over lead acetate.

These results show that the rate of evolution of the hydrogen sulfide increases with rise in temperature, and the last two results show that for a given temperature

²¹ *Kautschuk*, 2, 85 (1926).

the rate of evolution decreases with duration of heating. Here again it should be noted, however, that the results do not show the true rates of evolution of the gas for the several temperatures, since the same sample of rubber was used throughout the experiment, and was, therefore, already partly decomposed before being subjected to each of the individual tests.

Experiment 6.—Crude rubber was purified in the latex form and vulcanized as in the preceding experiment. About 40 g. of the vulcanizate were crumbled on the mill and digested for 6 days at 50° to 60° C., with frequent shaking, with a solution of 15 g. of potassium hydroxide in 600 cc. of alcohol. The alkaline solution was then replaced with a fresh solution of the same composition, and the digestion continued for 9 days more or 15 days in all. It was then digested at 50° to 60° C. with water for 20 days, the water being changed twice daily, then for 24 hours at room temperature with two successive portions of alcohol, dried in a vacuum at room temperature, and finally extracted with acetone for 3 days. The product then contained 7.13 per cent. of combined sulfur and 0.01 per cent. of nitrogen.

A portion of this material weighing 28.2 g. was heated in a stream of dry nitrogen, with results as shown in Table III.

TABLE III
THERMAL DECOMPOSITION OF VULCANIZED RUBBER*

Temperature, ° C.	Time of Heating, Hours	Amount of PbS Obtained, Grams	Temperature, ° C.	Time of Heating, Hours	Amount of PbS Obtained, Grams
25-30	48	0.0015	140	18	(**)
50	12	0.0010	140	16	0.0087
70	12	0.0015	200	6.5	0.0861
100	16	0.0032	200	20	(**)
120	12	0.0109	200	6.5	0.0195
140	15	0.0187			

* Weight of sample, 28.2 g. Combined S, 7.13 per cent.

** Not determined.

These results confirm in a general way those of preceding experiments, and lead to the same general conclusions. It should be noted, however, that a distinct test for hydrogen sulfide was obtained at room temperature, a fact which had not been observed in previous experiments. This is probably due to the fact that a longer period was allowed for action and that the proportion of combined sulfur in the rubber was higher than in most of the previous experiments.

After the above heating, the sample of rubber weighed 27.2 g. and contained 6.98 per cent. of sulfur.

Experiment 7.—Samples of the final product obtained in the last experiment were subjected to destructive distillation in an atmosphere of nitrogen. The rubber was placed in a large test tube through which a stream of oxygen-free nitrogen was passing, and heated carefully over a small free flame until the material first melted, then gradually charred, and at the end left only carbon and a heavy oil in the tube. The effluent gases were passed through an absorption tube containing lead acetate. Hydrogen sulfide was disengaged rapidly during the early part of the decomposition, so rapidly, in fact, that in some cases, when the heating was too vigorous, some of the gas escaped absorption even though two lead acetate tubes were used in series. In one such decomposition, 1.0233 g. of rubber, containing 6.98 per cent. of sulfur, yielded 0.2668 g. of lead sulfide, representing 0.0357 g. of sulfur, or 3.49 per cent. of the rubber sample. The lead sulfide was converted into barium sulfate in the manner previously described. The latter compound weighed 0.2595 g., or about 99.7 per cent. of the theoretical 0.2603 g. There is

reason to suspect that some of the hydrogen sulfide, though very little, escaped absorption in this case, the decomposition of the rubber having been accomplished in about one and one-fourth hours.

In a second determination in which the heating covered a period of about two and one-half hours, and in which all of the hydrogen sulfide was absorbed in the first lead acetate tube, 0.5020 g. of rubber yielded 0.1423 g. of lead sulfide, representing 0.0192 g. of sulfur, or 3.82 per cent. of the rubber sample.

It will be noted that in the last determination 54.7 per cent., or more than one-half of the sulfur in the rubber sample, was split off as hydrogen sulfide, but this rubber had already lost some hydrogen sulfide, in the preceding experiment, so that the real proportion of sulfur lost in this way was actually larger than the above results indicate.

Experiment 8.—Hard rubber made from pale crepe and sulfur, and containing about 30 per cent. of combined sulfur and 1 per cent. of free sulfur, was used for this experiment. When freshly disintegrated, as by means of a carborundum wheel or a steel rasp, the rubber evolved hydrogen sulfide at ordinary temperatures so copiously that it could be easily detected by its odor. Lead acetate paper suspended in a bottle containing a few grams of the hard rubber dust was discolored immediately, and was black after 10 to 15 minutes. The rate of evolution decreased rapidly, however, and after a week or 10 days the gas was coming off so slowly that the lead acetate paper was discolored only after two to three hours. At the end of four months, however, the powder still evolved the gas. The above behavior was observed not only in powder prepared from freshly vulcanized hard rubber, but also in that from hard rubber which was 4 months old.

A slab of hard rubber was heated for an hour at 100° C. under a pressure of less than 1 mm. and allowed to cool in this vacuum. When this rubber was converted into powder, the behavior as regards evolution of hydrogen sulfide was exactly like that already noted, so far as qualitative tests could show.

In the form of slabs, the hard rubber evolves hydrogen sulfide at room temperature much more slowly than in powdered form, but nevertheless continuously and apparently indefinitely. Two slabs of hard rubber, about 4 months old and weighing together about 150 g., when inclosed in a jar, discolored lead acetate paper appreciably in two hours.

A quantity of hard rubber was converted into fine shreds by means of a steel rasp, extracted with acetone for three days, or about 21 hours, and left immersed in acetone at room temperature during the three intervening nights, or 72 hours in all. It then contained 29.80 per cent. of sulfur.

Twenty-five grams of the extracted material were subjected to various temperatures in a stream of dry nitrogen, with the results given in Table IV.

TABLE IV
THERMAL DECOMPOSITION OF HARD RUBBER*

Temperature, C.	Time of Heating, Hours	Amount of PbS Obtained, Grams	Temperature, C.	Time of Heating, Hours	Amount of PbS Obtained, Grams
25-30	8	None	100	7	(†)
50	7	(**)	100	14	0.0053
75	21	0.0018	120	6	0.0574
100	18	0.0165	140	5	0.6348
140	3	0.5723	140	18	(†)
140	5	0.7258	140	5	0.3320
25-30	48	(†)			

* Weight of sample, 25 g. Combined S, 29.8 per cent.

** Barely perceptible.

† Not determined.

These results when compared with those of previous experiments show that the amount of hydrogen sulfide evolved increases with the proportion of combined sulfur. This is particularly noticeable at the higher temperatures.

After three months, the material which had been used in the above decomposition experiments was subjected to reduced pressure of about 28 to 30 mm. at room temperature for four days, during which air was frequently admitted in order to remove the accumulated hydrogen sulfide. It was then put into a tightly stoppered bottle and a strip of lead acetate paper was suspended within. The paper was distinctly discolored in 1 hour, light brown in 5 hours, dark brown in 24 hours, and black in 48 hours.

Experiment 9.—Some of the same hard rubber which was prepared for the preceding experiment, thoroughly extracted with acetone and containing 29.80 per cent. of sulfur, was subjected to destructive distillation in a stream of nitrogen, in the same manner as already described in Experiment 7 with soft rubber. From 0.2587 g. of the hard rubber, 0.3556 g. of lead sulfide was obtained, representing 0.0476 g. of sulfur, or 61.8 per cent. of the sulfur in the rubber sample.

In a second determination, 0.2599 g. of the extracted hard rubber yielded 0.3607 g. of lead sulfide, representing 62.4 per cent. of the sulfur in the rubber sample.

Experiment 10.—Two different stocks of soft rubber, one containing 3.71 per cent. of combined and 1.15 per cent. of free sulfur, the other containing 2.12 per cent. of combined and 2.70 per cent. of free sulfur, which had been vulcanized and then crumbled on the mill more than two years previously, and which had been kept in tightly closed, tinned cans, were still giving off hydrogen sulfide, as indicated by strips of lead-acetate paper suspended within the cans. The same results were obtained after these samples of rubber had been thoroughly aired by spreading them on a table for a week. To make certain that this hydrogen sulfide was not some which had been held in solution or absorbed in the rubber, 60-g. portions of each of these soft rubbers were extracted with acetone for two and one-half days, in the intervals of which the rubber also stood immersed in acetone during four nights and one and one-half additional days. When placed in closed vessels these extracted rubbers still discolored strips of lead acetate paper within three to four hours and turned them black within two to three days.

V. Discussion

It is evident that all vulcanized rubber is at all times disengaging hydrogen sulfide to a greater or less extent, at least at and above 25° C. This hydrogen sulfide is produced, at least in part, and in some cases unquestionably the greater part especially at elevated temperatures, by splitting off from the rubber-sulfur compound directly—not merely during, nor as a part of, the vulcanizing process, but after combination of rubber with sulfur has taken place. This is evidenced not only by the evolution of the hydrogen sulfide when there is no free sulfur present and the non-rubber constituents have been largely removed, but also by the fact that more than 60 per cent. of the combined sulfur in hard rubber can be thus removed. Of course, it is possible that under the conditions of destructive distillation the decomposition may follow a different course from that at lower temperatures, but this is not at all certain. The significant fact remains that the same product, hydrogen sulfide, is formed at all temperatures from 25° C. to the temperature of complete decomposition, considerably above 300° C.

The increase in the rate of evolution of the gas with rise in temperature or proportion of combined sulfur and its decrease with time at constant temperature, which have already been noted, are quite normal phenomena.

The influence of free sulfur and acetone-soluble non-rubber components has already been noted and adequately accounted for, although it is possible that these substances, as well as other impurities, may influence the results in still other ways.

Since the decomposition of the rubber-sulfur compound is going on continuously at and above ordinary temperatures, and since the rate of decomposition at constant temperature is continually decreasing it is obvious that the rate at which hydrogen sulfide will be evolved from a given sample of vulcanized rubber at any given time and temperature will depend to some extent upon the previous history of the sample and its condition or state of decomposition. For this reason the results obtained in any particular case are likely to be affected in a measure by the method of preparation or purification of the rubber sample, quite apart from the degree of purity attained. It is even possible that the degree of polymerization or depolymerization may have some influence upon this decomposition.

Since the decomposition of the rubber-sulfur compound takes place to an appreciable extent at the usual temperatures of vulcanization, it is at least partly responsible for the liberation of hydrogen sulfide during vulcanization. Furthermore, this splitting-off of hydrogen sulfide from the rubber-sulfur compound during vulcanization may result in additional unsaturation in the rubber molecule, which may presumably be saturated again by taking up more sulfur. This may account for at least a part of the excess of combined sulfur above the theoretical limit required by the formula C_2H_3S , as recently noted by Stevens and Stevens.

In the absence of sulfur this unsaturation may provide further opportunity for the addition of oxygen. Both the loss of hydrogen sulfide and its replacement by oxygen, if carried far enough, would certainly result in important changes in the properties of rubber. The evolution of hydrogen sulfide at ordinary or slightly elevated temperatures is very slow, but, because of the unknown losses of hydrogen sulfide occurring between vulcanization and testing, particularly during the process of purification, and because of other factors which have not yet been evaluated, the real change may be more important than the above results indicate. When such changes continue for months and years it is conceivable that their effect upon the properties of vulcanized rubber may be quite appreciable. The spontaneous decomposition of the rubber-sulfur compound would thus appear to deserve some consideration as a possible factor in aging.

Finally, since the spontaneous decomposition of the rubber-sulfur compound results in the removal from the rubber molecule of not only sulfur but also of hydrogen, this reaction presents another problem in the true regeneration of rubber from old vulcanized articles.

Fry and Porritt found that hydrogen sulfide is evolved from hard rubber at ordinary temperatures in diffused sunlight and air, due to the decomposition of the rubber-sulfur compound, and that the rate of evolution is increased by exposure to direct sunlight, as well as by a rise in temperature. These conclusions agree in the main with those reached in the present work, except as to the influence of light, which was not systematically investigated by the present writer.

That light should have some influence on this reaction is not unreasonable. Fry and Porritt, however, state that in the absence of light they were unable to detect any evolution of hydrogen sulfide. This does not agree with the observations of the present writer, since in the majority of experiments herein described the rubber was protected from light of all kinds. Nevertheless, the evolution of hydrogen sulfide from both hard and soft rubber, in total darkness, was repeatedly observed, both at ordinary and at elevated temperatures.

VI. Summary

It has been found that the rubber-sulfur compound in vulcanized rubber begins to split off hydrogen sulfide as soon as it is formed, and continues to do so at all temperatures between 25° C. and the temperature of complete decomposition of the rubber in destructive distillation above 300° C.

The rate of evolution of hydrogen sulfide from any particular sample of rubber depends upon the temperature, time, the proportion of combined sulfur, and possibly the condition of the rubber.

This reaction affords an additional explanation of the formation of hydrogen sulfide during vulcanization and, through the possible production of further unsaturation in the rubber, may afford a new explanation of at least part of the excess of combined sulfur over that required by the formula C_6H_8S .

The reaction may also be another factor in aging, and presents a new problem in the regeneration of rubber from old, vulcanized products.

Thermodynamics of Rubber.

I. Rubber as a System of Two Phases

L. S. Ornstein, [Miss] J. G. Eymers, and J. Wouda

In an earlier communication¹ v. Geel and J. G. Eymers published measurements, giving the elongation of raw rubber as a function of the stress per sq. cm. We have repeated the same measurements (Fig. 1) and have determined the changes of width and thickness simultaneously as a function of the stress. The sheets of rubber used in these and in the earlier measurements were prepared by evaporating latex, which had been poured on gelatin. This rubber had therefore not undergone mechanical treatment.

Further, in order to eliminate hysteresis as much as possible, a new piece was used for each measurement. The percentage reduction in the breadth and the thickness progresses in a similar way to that of the reduction in length as a function of the stress.

Now $E = \frac{dS}{d\left(\frac{\Delta l}{l}\right)}$ where l is the length and Δl the increase in length. Then,

$\frac{\Delta l}{l}$ is the elongation in per cent., S is the stress, and E is the modulus of elasticity.

If, therefore, we differentiate the extension curve, we obtain the modulus of elasticity as a function of the stress (Fig. 2).

Moreover, according to definition, $m \frac{\Delta b}{b} = \frac{\Delta l}{l}$, where $\frac{\Delta l}{l}$ is the extension in per cent., $\frac{\Delta b}{b}$ the reduction in breadth in per cent., and m is the contraction ratio.

Then $m = \frac{\Delta l}{l} \cdot \frac{b}{\Delta b}$; the curve giving $\frac{\Delta l}{l} \cdot \frac{b}{\Delta b}$ as a function of the stress differentiated, gives the modulus of contraction (Fig. 3).

We have already showed that the behavior of the extension past the point A (Fig. 1) might possibly suggest a new phase. As then expressed, the results of J. R. Katz in his Roentgen photographs of strained rubber give strong evidence in this direction. The constancy of E and μ after the stretch of 70 per cent. gives a further suggestion in this direction.

In the above-mentioned former publication, the connection between double refraction and stress was also measured, in which a dependence on the temperature was expected. This has now been measured and the results are plotted in Fig. 4. A dependence on temperature does not appear in the first portion, but does so in the second one, while the transition point A is displaced by change of temperature. This again suggests that rubber has a different structure after this point than before. Also the influence of the temperature on the extension was measured as a function of the stress.² The results are given in Fig. 5, and here one sees the dependence of the extension curve on the temperature. The transition point A is displaced by change of temperature in such a way that both the stress and the

extension of that point are displaced. The stresses of the transition point at various temperatures in Figs. 4 and 5 agree satisfactorily. As one works with

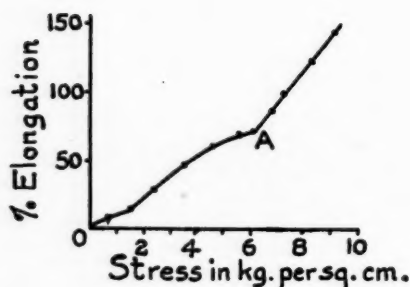


Figure 1

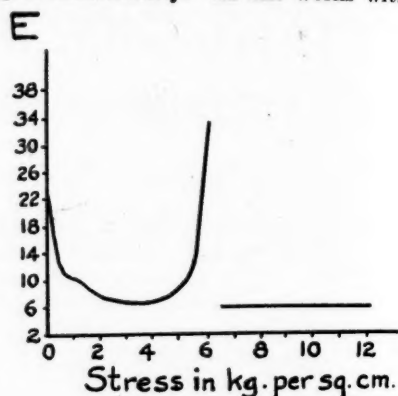


Figure 2

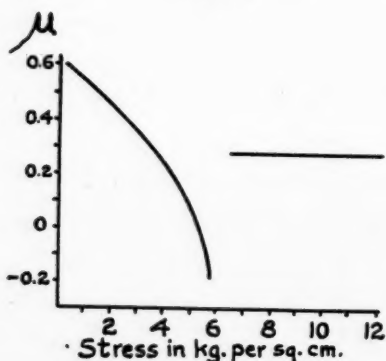


Figure 3

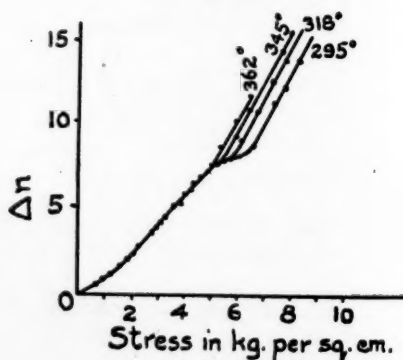


Figure 4

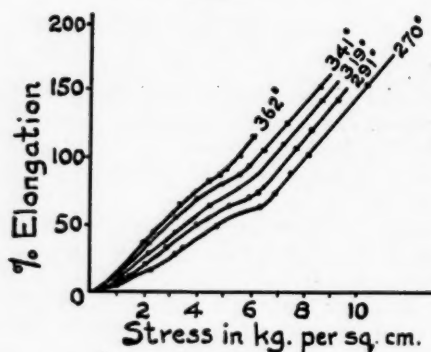


Figure 5

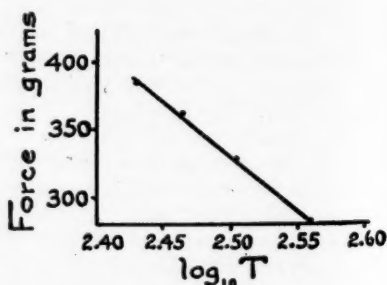


Figure 6

the force and not with the stress per sq. cm. in thermodynamics, we also plotted stress vs. force.

Now the Clapeyron equation for phase changes, in the form in which it is ap-

plicable to our case, gives $\frac{dK}{dT} = - \frac{r}{(l_2 - l_1)T}$, where K is the force which is acting on the cross section of the rubber, r = latent heat, and $l_2 - l_1$ is the increase in length for the unit of length. From the measurements it is apparent that, for the transition point, K is proportional to $\log T$ (Fig. 6), so $\frac{dK}{dT}$ is proportional $\frac{1}{T}$ which suggests a phase change (this is not a very important argument because, owing to the small temperature range, T is also approximately proportional to T). However, in the case of a phase change, it must be possible to show the change in length $l_2 - l_1$ for constant stress.

For this purpose a large number of measurements with a greater degree of accuracy were taken in the neighborhood of the transition point. For results examine Fig. 7. Here one can see that at that point the length undergoes a sudden change. Here, just as in the former measurements, a new piece of rubber was used for each observation. The fact that these pieces are never identical in composition, causes a rather considerable depression in the points. In order to avoid this difficulty, one should perform the whole series of measurements with one piece only. The difficulty of this, however, is that, as a result of hysteresis, the position

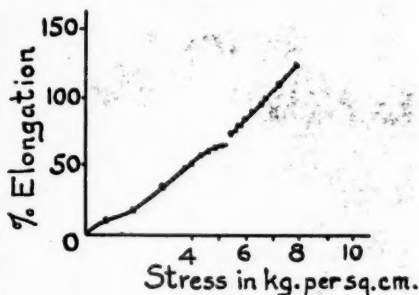


Figure 7

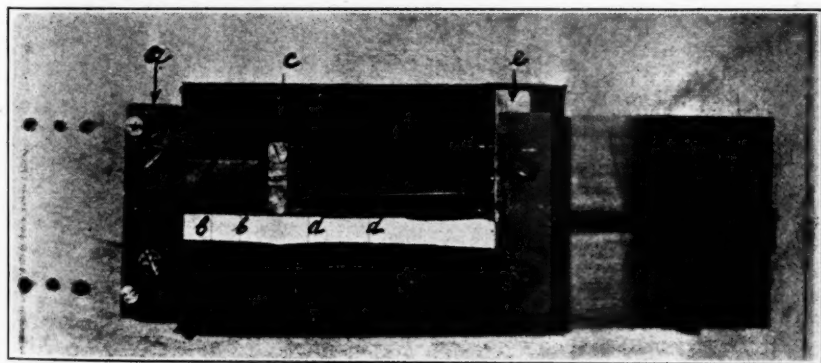


Figure 8

of the transition point becomes vague. Consequently the rubber must experience the whole range of extension from 0 to about 100 per cent. in a comparatively short period, while the force and strain acting on the cross-section simultaneously must be measured. An apparatus devised for the purpose rendered it possible. The apparatus (Fig. 8) is constructed as follows: a piece of rubber ($3 \times 1 \times 0.05$ cm.) is clamped at one end in a fixed clamp (a). The piece of rubber is provided with two pointers (b), rectangularly bent steel wires, pricked through the rubber. At the other ends the rubber is clamped in a small clamp (c), to which are fixed two spiral springs. The other ends of the springs are fastened to the clamp (e) to

which the drawing rod is connected. Pointers (*d*) are fixed to the clamps *c* and *e*, respectively. Portions of the pointers are illuminated by an automatic arc and a condenser lens. Another lens projects these needle parts on a rapidly rotating recording drum. With the aid of the drawing rod the rubber is strained to about 100

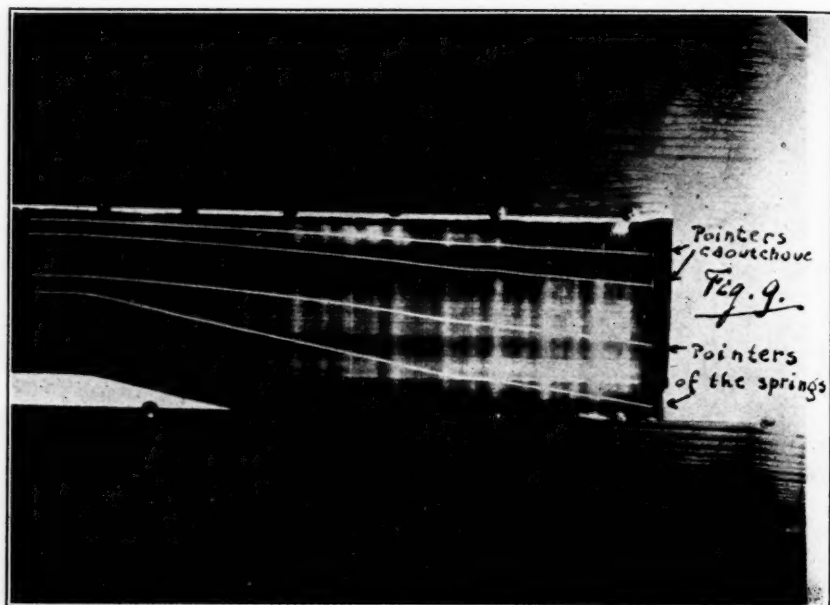


Figure 9

per cent. in about $\frac{1}{2}$ sec., while the distances of the indices apart are simultaneously recorded on the drum. Figure 9 represents a registration. The distance of the indices of the rubber represents the length and the distance of the indices of the springs the force. This method has the further advantage that the true transition

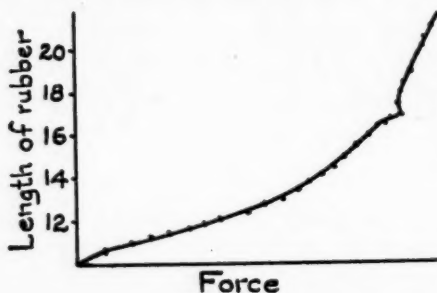


Figure 10

area is determined, which was not possible by the former method. Figure 10 represents the measurements of a registrograph where the extension is plotted as a function of the force in arbitrary units. This proves that there really is a phase change in the straining of rubber.

The initial portion of the curve before the transition area has a rather different form than the formerly obtained curve, which is to be attributed to the fact that we work under conditions less free from hysteresis.

After the transition area, the progress again becomes linear, even as in the former curves. The transition area occurs at a strain of approximately 70 per cent. which was also the case in former measurements. In connection with his findings of crystal interferences in rubber which was strained more than 70 per cent., Katz

has already expressed the opinion that in rubber the possibility of two phases exists which, however, gradually pass into one another.³ Now we find that the phases do not pass gradually one into another, but suddenly.

The average value of $l_2 - l_1$ was found to be 5 per cent. By means of this the heat of transition can be calculated, because:

$$\frac{dK}{dT} = - \frac{r}{(l_2 - l_1)T} K = - \frac{r}{(l_2 - l_1)} \log_e T + C$$

It follows from Fig. 6 that: $\frac{r}{l_2 - l_1} = 34 \times 10^4$. The heat per unit of volume is $17 \times 10^{-4} \text{ erg} = 4 \times 10^{-3} \text{ cal}$.

We have devised a scheme by means of which we hope to measure the heat of transition.

Beside this, one can read from Fig. 5 that the linear coefficient of expansion of raw rubber is positive. This fact is once more verified by the linear coefficient of an unstretched piece of rubber. According to the second principal law, this is directly contrary to the well-known fact that rubber becomes warmer on straining.⁴

The positive coefficient of extension must therefore cause a cooling effect on straining. The only explanation of a heating effect therefore lies in the hysteresis.

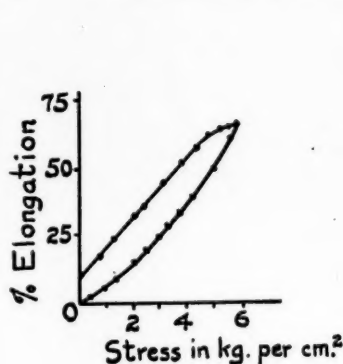


Figure 11

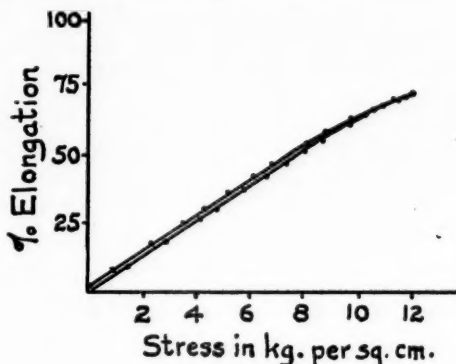


Figure 12

To check this, we then obtained a hysteresis curve of rubber by successively loading one piece more and more until the extension was about 70 per cent., and then gradually removing the load. Figure 11 gives the results. A similar curve can also be determined very conveniently by the apparatus shown in Fig. 8. Apparently the hysteresis is very appreciable. The overwhelming heat of hysteresis must therefore completely outweigh the expected cooling effect.

In the literature, one usually finds a negative coefficient of expansion for rubber, but in these cases commercial vulcanized rubber is used. In order to check this, we also measured the coefficient for a piece of commercial rubber and found it usually negative.

The hysteresis curve obtained for this rubber shows that the hysteresis is practically zero (Fig. 12). Here, therefore, the thermodynamics is to be tested, which will be communicated in a following article. Besides, the extension curve of vulcanized rubber was taken at room temperature by the registrograph method. From this it appears that this case is not a system of two phases occurring before the breaking strain, for there is no sudden change in length.

A systematic investigation of the influence of filling in this direction would perhaps lead to interesting results.

May we take this opportunity of thanking Dr. van Rossem heartily for his readiness to supply us with raw rubber.

References

¹ *Zeitschrift für physikalische Chemie*, Abt. B, 3, 240 (1929).

² As formerly a dependence of double refraction and extension on the thickness was already acknowledged (thanks to the surface layer), all measurements were done with rubber of the same thickness.

³ We believe the explanation of the fact that Katz finds not only crystal interferences, but also an amorphous ring when straining not very much above 70 per cent., to be as follows: his Roentgen photographs were taken with rubber that had been subjected to mechanical treatment; we have observed in former measurements that in this case the transition point becomes less distinct. Moreover, these exposures last several hours, during which the temperature does not remain constant and perhaps neither the strain. For this reason one can have the two phases at random, which explains the amorphous ring.

⁴ This generation of heat has been measured, and the results will shortly be published.

The Thermodynamics of Rubber

II. Temperature Change of Rubber under Adiabatic Stretching

D. S. Ornstein, J. Wouda, and [Miss] J. G. Eymers

In our first communication (*Proc. Acad. Sci. Amsterdam*, 32, 1235 (1929)) it was shown that the heating effect which takes place in stretched rubber must be due to hysteresis, because from thermodynamic considerations it is obvious that a substance with a positive coefficient of elongation shows a cooling effect. If this is true, rubber without hysteresis must obey the laws of thermodynamics. We have tested this for rubber of the following composition:

First latex sheet	100 parts	} Vulcanized 30 minutes at 147° C.
Sulfur	5 parts	
Diphenylguanidine	1 part	
Zinc oxide	3 parts	

which we got from Dr. van Rossem of Rijksrubberdienst, whom we heartily thank for his kindness also on this occasion. To determine whether this rubber is free from hysteresis, the following method was used:

A piece of rubber was successively loaded more and more, till the elongation was about 250 per cent., and then the load was gradually removed. No hysteresis was shown by the substance. When the rubber is submitted to a force which gives a change of length of this amount, the length of the rubber does not alter with the time. When, however, the elongation is more than 250 per cent., the length changes slightly with the time up to an elongation of 370 per cent.; beyond this elongation no alteration in length takes place again. When, in the case of these large extensions, the force is gradually decreased, the elongations come to much larger values than before, when the same force was applied to the rubber from its zero state. However, this is not an effect of hysteresis, for, however great the force and however long the time might have been during which the force acted (even more than 24 hours), the rubber always momentarily assumed its original length when the weight was removed at once. In Fig. 1 the areas from *O* to *E* and from *B* to *C* must be ascribed to different phases, and the difference between the graph for increasing and decreasing force can be explained by a retardation of phase. Moreover, the slope of the curve *AB* can be much steeper as in this case, with a longer time between the application of different forces. Further, the rubber in the region *DE* is not in a stable state, for a slight impulse affecting the rubber causes the elongation to decrease at once. Since the second phase already shows itself above an elongation of 200 per cent., we have taken all our readings for thermodynamic relation below that elongation. It is known that from thermodynamical considerations one can get the formula for the change in temperature:

$$\Delta T = - T \int_0^{\Delta l} \frac{\left(\frac{\partial S}{\partial l}\right)_T \cdot \left(\frac{\partial l}{\partial T}\right)_S}{\left(\frac{\partial \epsilon}{\partial T}\right)_l} dl$$

where *T* is the absolute temperature during the measurement (ΔT is small com-

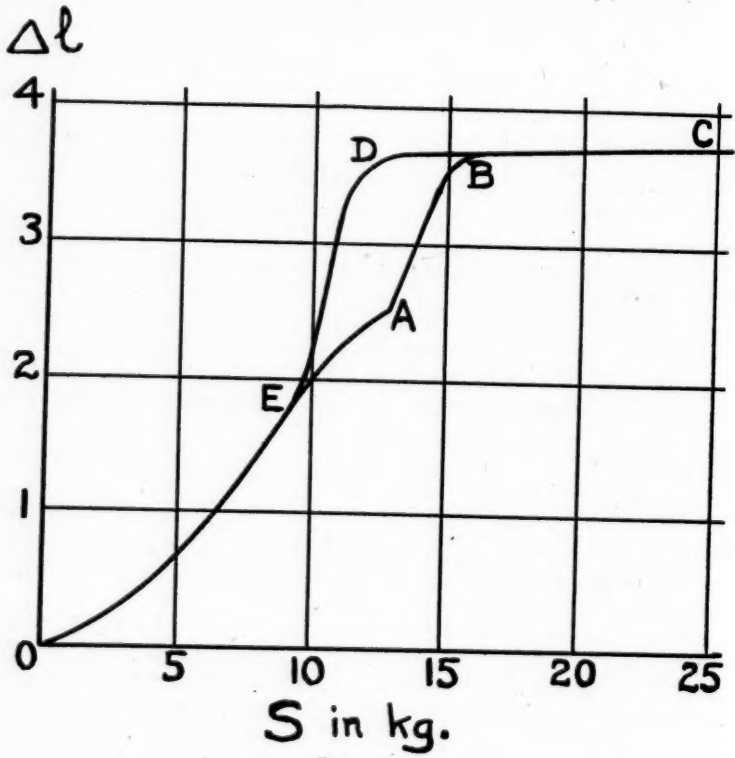


Figure 1

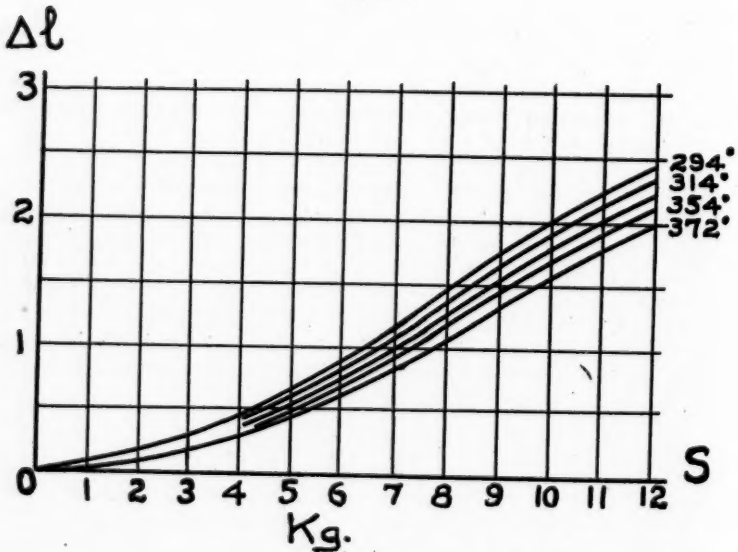


Figure 2

pared with T), S is the force and ϵ the energy and thus $\left(\frac{\delta \epsilon}{\delta T}\right)_l$ the specific heat by constant length per cu. rubber. In order to test this relation, the length must be measured as a function of the force at different temperatures. From the curves, giving this (Fig. 2), we can deduce $\left(\frac{\delta S}{\delta l}\right)_T$ and $\left(\frac{\delta l}{\delta T}\right)_S$; besides the dynamical qualities, the specific heat as a function of the elongation has been measured (Fig. 3). The S - l curves were determined in the same way described in our first communication loading a piece of rubber with different weights and measuring the length with a cathetometer. The rubber is placed in an oven which could be brought to the desired temperature by electric heating. During a series of measurements the oscillations of temperature were less than 2° . The results are plotted in Fig. 2. The temperatures used are 294° , 314° , 334° , 354° , and 372° K.

The measurement of the specific heat was somewhat more difficult, as a result of the very bad conduction of heat by the rubber. Finally the following method

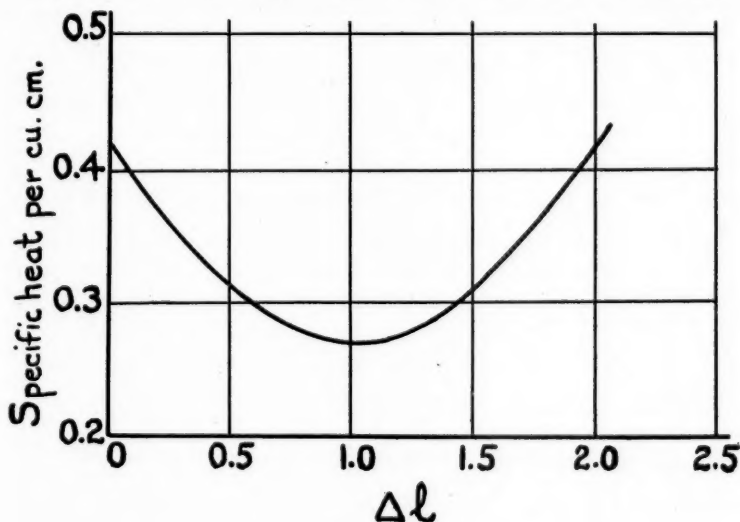


Figure 3

was adopted: small rings were stamped with a diameter of about 2 cm. and a breadth of 1 to 1.5 mm. This form of the pieces of rubber was chosen for two reasons: first, in order to make the surface as great as possible (in this way we got a better conductivity of heat with the same mass of rubber); and, further, in order to get a simple way for measuring the stretched rubber. The rings were stretched on plates of brass of different lengths, which were bent in the form of a cylinder to occupy as small a space as possible. The cylinder of brass with rubber was heated in an electric oven up to about 80° C. (the oven was kept at this temperature during an hour) and then brought into a calorimeter, turning the furnace quickly. The calorimeter was constructed as follows: A vacuum tube of U-form was placed in a water bath of constant temperature. The lower part of the tube was filled with mercury. In the small branch a thermometer was placed in the mercury, which could be read off to a fiftieth part of a degree through the unsilvered portion of the tube, by means of an eyepiece.

Above the mercury in the wider arm were 40 cc. of distilled water, into which the warm cylinder of rubber was placed. A wire was fixed to the cylinder, which could be moved up and down by a small motor; the rubber itself thus acting as a stirrer. This form of calorimeter had the advantage that the volume of liquid was

$$I \times 10^4$$

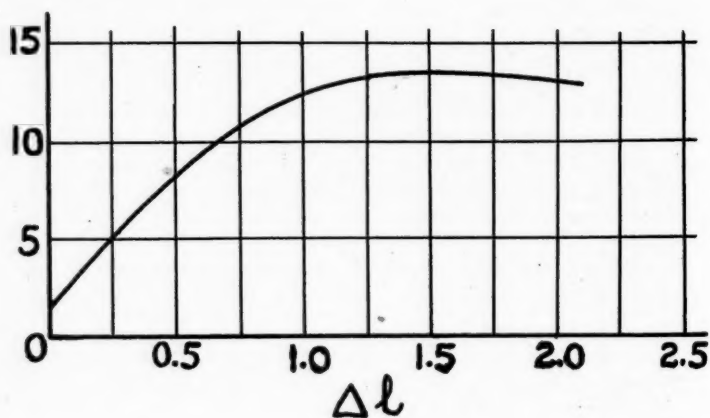


Figure 4

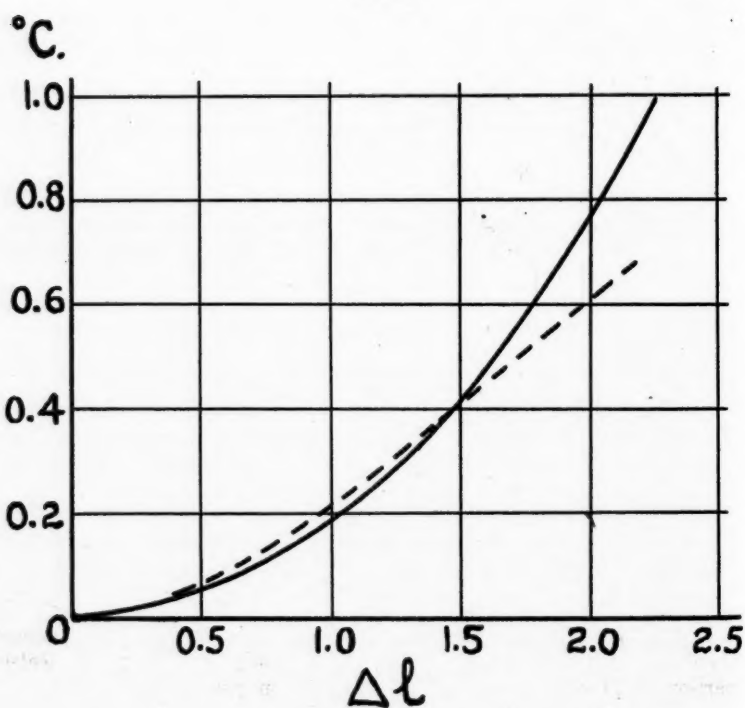


Figure 5

as small as possible in comparison to the mass of the rubber and therefore the rise of temperature in the calorimeter was as large as possible. We got in this way a maximum rise of the temperature of two degrees. Before and after the rubber was placed in the calorimeter, the change of temperature was observed during about an hour, in order to determine the corrections necessary for the gain or loss of heat to the surroundings. The effective water equivalent of the calorimeter was determined as a function of the volume of the material with which it was filled; it appeared to increase with that volume. The change of the specific heat per cc. as a function of the elongation is given in Fig. 3. Apart from the investigation of thermodynamical equation the form of the curve for the specific heat is most interesting, as the great variation of this quantity with the elongation must be of utmost importance for the understanding of the molecular state of rubber. The specific weight of this rubber, necessary to calculate the specific heat per cc., was 0.915. From the results given in Fig. 2 we can calculate $\left(\frac{\delta S}{\delta l}\right)_T$

and $\left(\frac{\delta l}{\delta T}\right)_S$ as a function of the extension. The curves obtained are multiplied with each other and divided by the curve giving the specific heat per cc. as a function of the elongation where all functions are expressed in C. G. S. units. The resulting curve is given in Fig. 4.

$$I = \frac{\left(\frac{\delta S}{\delta l}\right)_T \times \left(\frac{\delta l}{\delta T}\right)_S}{\left(\frac{\delta e}{\delta T}\right)_l}$$

The area between this curve and the axis was measured with a planimeter for different elongations and multiplied with the absolute temperature at which the generation of heat had been measured (ΔT is a positive because $\left(\frac{\delta e}{\delta T}\right)_S$ is negative).

In order to test the thermodynamics, the generation of heat itself ought to be measured, which was done by the method described below.

A thermocouple of copper-constantan was sewed in a piece of rubber in the direction in which the displacement of the material along the thermoelement was as small as possible when the rubber was stretched; in that way the generation of heat caused by friction was reduced to a minimum. The other contact of the thermocouple was plunged in a thermoflask filled with water, the temperature of which was absolutely constant during each measurement. The thermoelectric force was measured with a Moll galvanometer, in the circuit of which was placed an arrangement for measuring the sensitivity for changes of potential. The rubber was clamped in a box between a fixed and a movable clamp. To the movable clamp was fixed a drawing rod, the end of which projected from the side of the box, and to which was also fixed a stop, by means of which the rubber could be stretched to a given length. The elongation was determined with a cathetometer, just as in the case of the measurements for the S - l curves. The time of elongation was small compared with the time which the galvanometer took for its deflection. This deflection of the galvanometer was registered during the adiabatic strain and also for a few minutes after. By extrapolation, the influence of inertia of the galvanometer and loss of heat to the surroundings could be eliminated. The time necessary for the thermocouple to assume 99 per cent. of the temperature increase of the rubber was calculated to be of the order of $1/6$ sec., i. e., it can be neglected in comparison with the time necessary for the galvanometer to come to its maximum deflection. The maximum error due to losses of energy by the thermocouple

itself was, as calculated, 4 per cent. The values for the increase on temperature got from experiment and from the theoretical formula have been plotted in Fig. 5. The observed and calculated points are indicated by the signs + and 0, respectively. Up to an elongation of 150 per cent. the agreement is satisfactory. Above this elongation the observed rises in temperature are higher than those calculated from the thermodynamical formula. This difference can easily be explained by the influence of the second phase, which shows itself appreciably above an elongation of 150 per cent., as Fig. 1 shows.

As was pointed out in our former publication, the generation of heat by stretching raw rubber was measured. It was expected that the generation of heat at the transition point would show an abnormality owing to the heat of transition.

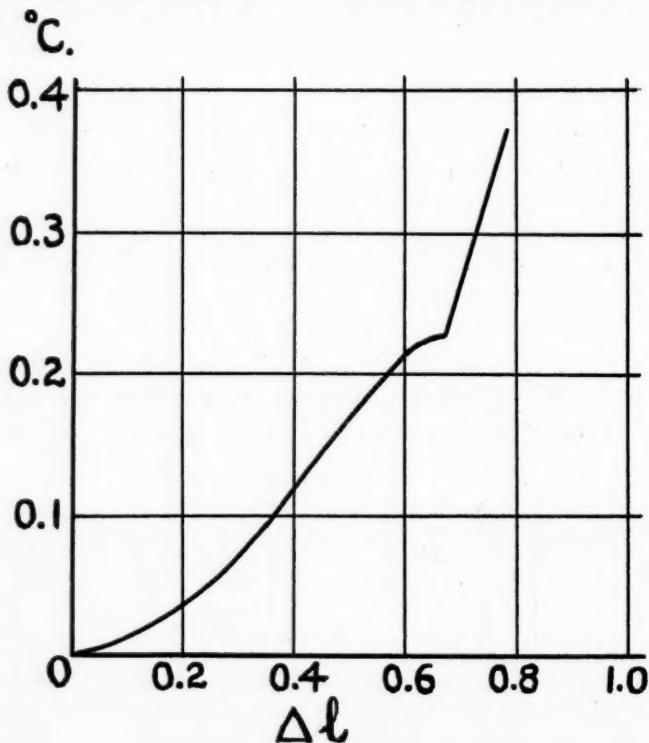


Figure 6

For this reason an amplifier method was used to measure the temperature with greater accuracy.

The copper-constantan thermocouple was placed between two pieces of raw rubber. New pieces were used for each measurement in order to eliminate the influence of hysteresis as much as possible. The measurement took place as described above for the measurement with vulcanized rubber. The results are plotted in Fig. 6. This curve has the same form as the curves for double refraction and elongation as a function of the tension given in our former paper. Beyond the transition point, that occurs at an elongation of about 70 per cent.; the rise in temperature increases linearly with the length. Further measurements are planned in order to find the relation between hysteresis and heat development.

The Solvation of High Molecular Substances, Especially Rubber

P. Stamberger and C. M. Blow

In order to decide the size of the molecules, substances of high molecular weight were studied with respect to the combinations which they form with solvents, disregarding purely chemical investigations. Conclusions can be drawn from these experiments only when the laws governing the union of solvent and solute are accurately known.

Until recently opinion has been pretty much divided¹ as to the nature of the union with solvent. It now appears that the process must be interpreted as an actual combination of the two, and, therefore, either the solvent penetrates into the capillaries or else is adsorbed on the surface of the molecular aggregates, the micelles. These views have already been advocated by van Bemmelen² who says: "All this indicates that the combined water is retained by the smallest particles or molecules and completely pervades them on reabsorption. Thus the power to combine with water is not a function of the larger particles but of the smallest ones. The phenomenon is not an adsorption but an absorption."

Later the same view was expressed by Katz³ as follows: "The extensive analogy between swelling and solution, as shown in the preceding chapters, justifies the assumption that both phenomena are essentially very closely related. I believe that we will best understand this analogy if we conceive of swelling as the formation of a solution of water in a body capable of swelling." In the footnote he says that this conception has been voiced before in several quarters, but has not been generally accepted, due to lack of experimental data.

This view has been recently advocated by Staudinger.⁴ To be sure he goes further in his conclusions than the authors named above. He says, "These high molecular substances go into solution in the same way as those of lower molecular weight. The solvent penetrates between the molecules and surrounds them with a film of solvate. Then we believe, in contra-distinction to other authors, that a layer of solvent molecules, perhaps monomolecular, is held fast, just as in the case of simple homopolar molecules, for we correlate this solvation of homopolar molecules with adsorption." Further he says, "The process of solution is, however, extraordinarily affected by the length of the molecules. Solubility is known to decrease with increasing molecular weight, and this is true of series of homologous polymers as of series of homologs. In the case of solid macromolecular substances, the process of solution—that is, the dissolution of the individual molecules at the surface in contact with the solvent—is so slow that molecules of the liquid find time to penetrate far into the material. Thus large quantities of solvent become lodged between the individual molecules, so that the latter are pushed apart and swelling sets in before the molecules at the surface are completely dissolved. On the other hand, in the case of substances of lower molecular weight, the molecules at the surface are quickly dissolved before the solvent finds time to penetrate the substance, and thus normal solution takes place."

Staudinger also maintains not only that the molecules are surrounded by molecules of solvent, as is also believed by others, but that they are distributed in the excess solvent in molecular disperse form. Thus, after a sufficiently long time when all the molecules become completely solvated, a molecular disperse solution

should be formed. Likewise any dependence between the solvated particles should no longer exist. As in the case of smaller molecules, solutions would be obtained, which, when dilute, would show the decrease in the activity of the solvent (measured by the lowering of the vapor pressure and osmotic pressure and the changes in the melting point and boiling point) proportional to the number of molecules. This theory is also said to be applicable to rubber.⁵

Staudinger expressly denies the existence of structural features in a liquid or aggregation in the case of homopolar substances such as rubber, provided that the concentration of the solution is not too high. He says,⁶ "These experiments indicate that these anomalous viscosity phenomena in the case of a homopolar

macromolecular colloid are not to be ascribed to any structural feature of the liquid or to aggregations but rather depend on the length of the molecule."

Now it seems appropriate to discuss these views, partly on the basis of some experimental results, partly on the basis of the opinions of others who have worked on the matter.

The molecular nature of the union with solvent in the swelling of rubber was pointed out by one of the authors not long ago.⁷ In measuring the depression of the vapor pressure by various samples of rubber, the extraordinarily interesting fact was discovered that samples from different sources gave the same values. Even samples of masticated rubber behaved the same way. However, if the curve showing the relation between the depression of the vapor pressure and the concentration is compared with that of a substance of lower molecular weight, very large differences are apparent.

In the case of substances of low molecular weight such as cane sugar, the relative depression of

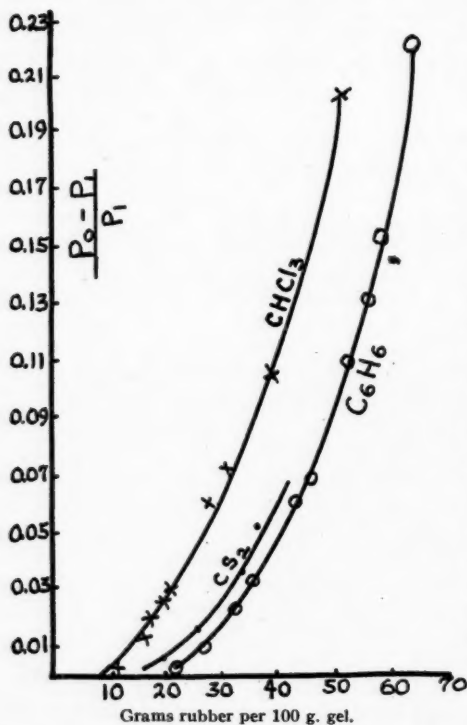


Figure 1

the vapor pressure is directly proportional to the concentration up to a value of 50 per cent.⁸ In the case of rubber no linear portion can be found at all. As shown in Fig. 1 the curve bends immediately very much toward the axis representing the depression of the vapor pressure. It is also evident that measurable depressions can be found only below a definite concentration. Hence the conclusion was drawn that the solvent loses considerable of its activity when it enters the sphere of attraction of the dissolved molecule. The thickness of the solvent layer in those cases where the lowest depressions were found by measurement was calculated as roughly 1.5 to 2 Å. U. These results were in accord with Staudinger's (*loc. cit.*) theory, published at about the same time, that molecules of jellies are surrounded by a film of solvate whose thickness is approximately

monomolecular. To be sure Staudinger does not state on what experimental data he came to base these conclusions.

As previously mentioned, rubber test pieces of different origin gave the same values. In the work cited three samples of rubber were examined which came from wholly different sources, were of different age, and had received different handling on the mill. If they represented mixtures of various degrees of polymerization, then such behavior could hardly be expected. In this connection the fact may be mentioned that Ruhemann and Simon⁹ when measuring the specific heat of various rubber fractions at various temperatures could find no difference in their behavior. The contradiction of these results with the theory of Staudinger has been pointed out by one of the authors.¹⁰

Measurements of the tendency to swell gave the same result, even using rubbers of different origin. The values obtained could to some extent be compared with those of Posnjak,¹¹ and, considering the difference in technic, afforded a very good agreement. Posnjak's values were obtained eighteen years ago with unpurified Para rubber. It would be extremely remarkable if the quantity of various polymeric homologs were always the same in various rubbers. Rather rubber is a very definite substance, as believed by Harries and recently proposed anew by Pummerer, Nielsen, and Gündel.¹² This contradicts Staudinger's conception, according to which rubber consists of a mixture of polymeric homologs.¹³

The methods used in these measurements and the results obtained have not been described as yet, so that it seems purposeful to do so briefly. The apparatus used in measuring the swelling tendency was somewhat different from that of Posnjak. The latter used a perpendicular tube, 10 cm. long, on which the clay cell serving as semi-permeable membrane was fastened.¹⁴ The substances to be swollen were therefore under a constant pressure of 10 cm. of mercury, which was not taken into account in the measurements. The data given for comparison with the authors' measurements take this error into consideration.

Figure 2 shows the apparatus used. The semi-permeable membrane, *A*, consists of a porous porcelain plate impregnated with a rubber solution according to Caspari's method and then cold vulcanized.¹⁵ This membrane is wholly impermeable to rubber, but is permeable to the solvent. The rubber test pieces under examination are weighed out into the glass cell, *B*, whereupon the membrane is fastened to the flanges of the cell with water glass. The whole apparatus was then placed in an air bath maintained at 25° C. and filled with mercury free from air by connecting *E* with a mercury bulb. The exit tube, *D*, was at the same height as the membrane and the rubber, which, of course, rested on the mercury. (The membrane was suitably fitted to the upper part of the cell for this purpose.) The excess mercury was drawn off by opening *D*. In this way the whole apparatus is filled with mercury without being under pressure. Toluene, the solvent used for swelling, was now poured into the outer cylinder, *F*. On swelling, the rubber extruded through *D* a quantity of mercury corresponding to its increase in volume, which was caught and weighed. The increase in volume, and therefore the concentration of the rubber in the gel, was calculated from the weight of the mercury.

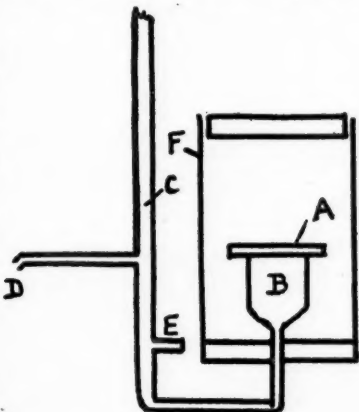


Figure 2

On closing *D*, pressure is exerted by the mercury bulb through the column of mercury in the manometer, *C*. The fall of the mercury meniscus corresponds to the deswelling produced by the pressure. In this way observations are made of the swelling pressure or better the solvation pressure depending on the concentration.

It was of further importance to determine whether the rubber swollen and deswollen in this way was of uniform concentration or not. In the case of unmilled rubber this was always so, but in the case of milled rubber this was not the case at all, so that other apparatus had to be used for measurements of this nature. A report will be made elsewhere on this matter and on the theoretical significance of the measurements.

The values obtained with unmilled rubber are given in Table I, and in Fig. 3 they are compared with those obtained by Posnjak. These values show that, although the combination of the rubber with the solvent is a molecular process, it takes place in a manner entirely different from that of smaller molecules. No

TABLE I

Rubber Sample I	Swelling Pressure (g. per sq. cm.)	Concentration (g. rubber per 100 cc. of jelly)
Measurement 1	150	7.4
	184	7.73
	226	8.07
	267	8.45
	320	9.03
Measurement 2	417	9.45
	485	9.65
	531	10.10
	605	10.40
	702	11.9
	826	11.90
Measurement 3	392	9.50
	503	10.0
	720	11.30
Measurement 4	334	9.54
	266	8.03
	184	7.53

portion of the curve is in accord with the van't Hoff equation. Therefore in the case of rubber the solvent is held by forces quite different from those present in solutions of similar concentration where the osmotic pressure is proportional to the concentration.

Measurements of the osmotic pressure of solutions of rubber and of similar substances have not shown any applicability of the van't Hoff equation. An attempt was made to apply corrections so as to find a possible way of determining the molecular weight,¹⁶ but none of the methods tried were considered of experimental significance. This question will be discussed elsewhere. In carrying out molecular weight determinations based on Raoult's law, care must be taken that the conditions on which this law is based are fulfilled. Staudinger and his co-workers found them fulfilled in the case of the synthetic products which they examined. At various concentrations they found the same relative depression of the freezing point. This is not so with rubber. Here no depression of the freezing point is found, and the osmotic pressure shows no linear dependence on the concentration.

This behavior during solvation affords no grounds for the assumption that rubber goes into solution in the same way as substances of lower molecular weight.¹⁷ On the contrary one can say with certainty that this is not the case.

According to Staudinger the fact that solutions with ultramicroscopic particles cannot be formed indicates that a molecular dispersion takes place. He says:¹⁸ "The long threads of colloidal molecules in solution on the contrary do not appear ultramicroscopic if one works with pure synthetic products which can be obtained optically empty." Solutions of unmilled rubber were also found to be optically empty.¹⁹ Dead milled rubber will give ultramicroscopic solutions at least in part

(Klein and Stamberger, *loc. cit.*). It can even be shown macroscopically that in the case of dead milled rubber there is a stronger Tyndall effect than in the case of the same rubber that has not been milled. This is also the case if all impurities introduced during the milling operation are removed from the dilute solution by centrifuging strongly. However, this does not show that no aggregates of strongly solvated molecules can be present in solution. They cannot form ultramicroscopic solutions any more than molecules uniformly dispersed. The fact that molecules or parts of molecules are solvated has been frequently stated by others.²⁰ Sheppard and Houck (*loc. cit.*) have shown that, when cellulose acetates are treated with a mixture of solvents, a breaking down of the aggregates occurs, accompanied by a decrease in viscosity and plasticity, the latter term being used in the same sense as the structural viscosity of Ostwald. It is striking that the sol-rubbers of Pummerer yielded solutions of extremely low viscosity. However, to draw any conclusion from this behavior as to the molecular distribution would be premature.

In connection with the viscosity of these solutions it may be pointed out that Staudinger and recently

Fikentscher and Mark²¹ draw conclusions as to the molecular weight of the dissolved phase based on these measurements. Staudinger maintains that the reason for the decrease in viscosity of solutions of rubber previously milled is depolymerization. "Such cleavage or destruction of the long chains also occurs during mastication, where it must be assumed that a rupture of the carbon linkages takes place. This rupture of the carbon chains occurs

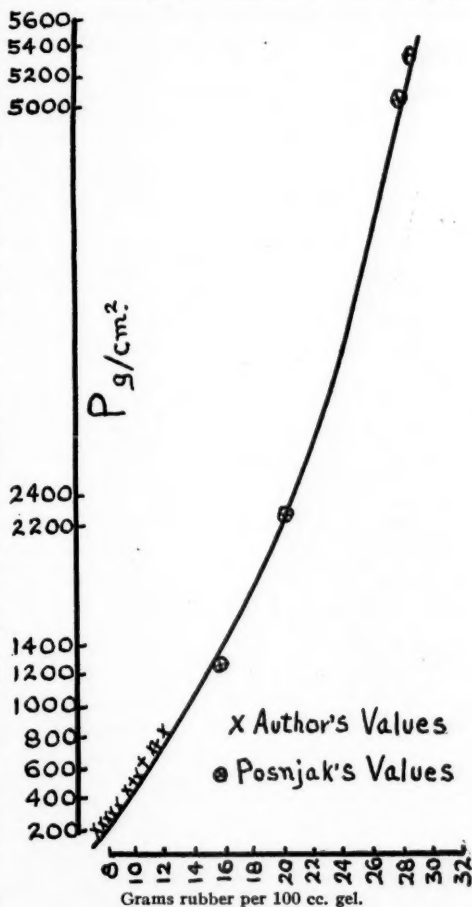


Figure 3

purely mechanically, just as the normal valences between the carbon atoms in diamonds can be overcome by mechanical forces."²²

This conclusion is also reached by Fikentscher and Mark.²³ They believe, for example, that the molecular weight of rubber is decreased by milling to one-third the original.

It has already been pointed out that the measurements of the depression of the vapor pressure with milled and unmilled rubber were the same. The measurements of the solvation pressure of dead-milled rubber available at present show no difference from the values obtained with unmilled rubber. Fairly weak solutions of rubber in toluene were examined, and at a concentration of 10 per cent., for example, were quite mobile. The difference between the swelling pressures of milled and unmilled rubber reported by one of the authors²⁴ was due to an error in technique, for the absorption of fluid by dead-milled rubber with the apparatus described did not take place to the same extent at different heights. The diffusion of the solvent into the layers farthest from the membrane appeared to occur extremely slowly. Even after six months the concentration of these layers differed. Hence, in measuring the swelling pressure, the attainment of equilibrium was taken wrongly, for on account of the extremely slow diffusion the pressures for a long time produced a change of volume only in the outer layer. The values obtained were therefore easily reproducible. Strange to say, this is not the case using unmilled rubber. Therefore, other apparatus had to be used, in which the concentration of the rubber solution did not change throughout the experiment.

This behavior did not indicate the occurrence of any depolymerization. The assumption that there is a connection between the viscosity of a solution and the molecular weight of the dissolved substance is not founded on theoretical grounds, and the present data lead us to doubt the correctness of such a view. Furthermore, it was found that compounds of gas black and dead-milled rubber behaved in such a way as regards viscosity that they could hardly be brought into agreement with the dependence on the molecular weight suggested by Staudinger, Mark, and Fikentscher. This matter has been briefly reported elsewhere by Blow. It was possible to show that the viscosity of solutions of overmasticated rubber containing increasing quantities of gas black increased with the content of black. Table II shows this increase in compounds prepared shortly after the milling process.

TABLE II

Concn. of Solution (g. rubber per 100 cc. of solution)	Per cent. by Weight of Gas Black	Relative Viscosity (Benzene = 1)
2.5%	2.5	4.64
	5	5.25
	7.5	5.15?
	10	6.86
	15	7.75
10 %	2.5	68.3
	5	86.0
	7.5	95.0
	10	105.0
	15	238.0

This table shows that the increase is relatively greater in the case of concentrated solutions (10 per cent.).

If the solutions were prepared some time after milling, a marked increase in viscosity was evident. It has been pointed out by one of the authors that rubber compounds containing larger quantities of gas black go into solution shortly after milling.²⁵ If they are allowed to stand some time after milling, they no longer

swell without limitation. Moreover, an increase in the tensile strength of these compounds can be shown after some time. Compounds which, shortly after milling, possess the plastic properties of overmasticated rubber become firm and elastic on aging. This change was followed by observing the viscosities of solutions prepared.

The change in viscosity of such compounds one month after milling is shown in Table III.

Concn. of Solution (g. rubber per 100 cc. of solution)	TABLE III Per cent. by Weight of Gas Black	Relative Viscosity (Benzene = 1)
10%	2.5	97.92
	5	127.0
	7.5	140.0
	10	150.0
	15	257.0

The interesting fact was discovered that these solutions showed thixotropic behavior to a high degree. The viscosity changed if the solution was poured repeatedly through the capillary of the viscosimeter, and especially on shaking. The values given are final values obtained after shaking.

It is of further interest that this behavior can be made to agree with McBain's explanation of the reinforcing action of fillers, namely, by the assumption of an orientation around the filler of the adsorbed rubber particles,²⁶ an elastic structure resulting in consequence. This orientation is effected by the gas black particles. This behavior likewise agrees with the explanation of the mastication process by Klein and Stamberger,²⁷ which assumes that mastication effects a destruction of the framework, that is, a destruction of the regular orientation of the rubber molecules. In this way the change in the elastic structure during milling is explained. If a new orientation is effected by the gas black particles, the elastic properties are increased by the vectoriality of the intermolecular forces. This is shown by the solutions, which are more viscous and also thixotropic. In the same way a decrease in the plasticity of the compounds was demonstrated.

It is well known that solutions cannot be made of mixtures containing high quantities of gas black. Their swelling is only of the "limited" type. In the course of time a portion of the rubber does diffuse out, but this diffused rubber has the same viscosity as that originally used. This fact completely excludes the possibility of the action of the gas black being a polymerization. Therefore, the change in the viscosity of rubber after various treatments is not due to any depolymerization, but merely to a change in structure or orientation of the rubber particles. Therefore the molecular weights of such substances can hardly be determined by viscosity measurements.

From the experimental data given above it is evident that the question as to how the particles of rubber and rubber-like substances are distributed in solution must be considered as wholly unsolved. Moreover, measurements with so-called monomolecular layers tell us nothing on this point. In recent years it has been shown that high molecular substances spread out when in solution in the form of a thin layer of molecular dimensions. This was shown with mercury by Sheppard and Keenan²⁸ and with water by Knight and Stamberger²⁹ and by Katz and Samwell.³⁰

The thickness of such layers under certain conditions corresponds to one dimension of the molecule. Of course, measurements of this sort tell us much concerning the structure of the molecules, but, on the other hand, nothing about the form in which they are distributed in solution. The spreading out of these particles

on the surface tells us nothing more than that the forces of attraction of the free surface of the fluid (water or mercury) upon certain polar groups of the spreading molecules are greater than the forces of attraction between the molecules themselves. A drop of oleic acid, though not dissolved, will also spread out.

There are data available which indicate that the distribution of such substances in solution is of an extremely complicated nature. For example, it has been found³¹ that the solvent is not without effect on the molecular size of the substance dissolved. It has been shown that the molecular weight of vulcanized triolein obtained cryoscopically is lowered by treatment with solvents at high temperatures. The residue on evaporation is much different in consistency and elasticity from the original material which was dissolved, and, moreover, immediately after it was obtained it went into solution easily. Recently Fuchs³² noticed a similar behavior in the case of the decomposition of lignin by methylglycol and hydrochloric acid, and proposed the following theory in explanation. "Natural products of high molecular weight sometimes behave in such a way that one is compelled on stoichiometric grounds to assume a relatively low molecular weight; but at other times they behave in such a way that one must consider them as structures which probably consist of a union (*e. g.*, chain-like) of simple and similar structural units. We have avoided the assumption of a decomposition and recombination in solution of substances of high molecular weight, yet this is what I consider as very probable. Just as salts decompose into ions, I believe that high molecular compounds can decompose into 'reactals,' the latter being a new term used for description and calculation, and signifying an atomic grouping of two-fold value which is distinguished from a molecule by its unsaturated character and from an ion by its electrical neutrality. Facts apparently contradictory may be explained by assuming that the stoichiometric molecules or structural units of high molecular natural products have all the properties of small molecules and also other properties which determine their peculiar nature."

Experimental confirmation of the fact that such products of dissociation are present in solution is not available, and it has been hardly observed that the products in solution possess properties other than those of the base molecule. This is particularly the case in organic solvents, since dissociation often occurs in water. However, it is interesting to indicate this trend of thought.

Conclusion

1. On the basis of new experimental data on rubber, the theories of the solvation of high molecular substances are discussed.
2. In this discussion the measurements of the swelling pressure of rubber in toluene are described. The values obtained, and also the measurements of the depression of the vapor pressure lead to the conclusion that rubber cannot be considered a mixture of homologous polymers.
3. The consistency or viscosity of gels is without effect on the decrease in the activity of the solvent (measured by the depression of the vapor pressure and the swelling pressure).
4. The conclusion is drawn that mastication cannot be considered a depolymerization.
5. On the basis of measurements of the viscosity of solutions of rubber-gas black compounds it follows that conclusions as to the molecular weight of the dissolved phase cannot be drawn from viscosity measurements without further ado.
6. The theories of the distribution of high molecular substances in solution are briefly discussed.

Notes

- ¹ Freundlich, "Kapillarchemie," p. 323.
- ² *Z. physik. Chem.*, **24**, 244 (1897).
- ³ "Gesetze der Quellung," Dresden, 1916, p. 156.
- ⁴ *Ber.*, **62**, 2903 (1929).
- ⁵ Staudinger and Bondy, *Ber.*, **62**, 2413 (1929).
- ⁶ *Ber.*, **62**, 2928 (1929).
- ⁷ *J. Chem. Soc.*, 1929, 2318.
- ⁸ Berkeley and Hartley, *Proc. Roy. Soc. (London)*, **77A**, 156 (1909).
- ⁹ *Z. physik. Chem.*, **138**, 1 (1929).
- ¹⁰ "Colloid Chemistry of Rubber," Oxford University Press, 1929, p. 76.
- ¹¹ *Kolloidchem. Beihefte*, **3**, 417 (1912).
- ¹² *Ber.*, **60**, 2167 (1927).
- ¹³ *Ibid.*, **61**, 2575 (1928), and elsewhere.
- ¹⁴ *Loc. cit.*, p. 422.
- ¹⁵ *J. Chem. Soc.*, **105**, 2139 (1914).
- ¹⁶ Meyer and Mark, *Ber.*, **61**, 1946 (1928); Kroepelin, *Kolloid-Z.*, **47**, 297 (1929); Ostwald, *Ibid.*, **49**, 60 (1929).
- ¹⁷ Staudinger, *Ber.*, **62**, 2903 (1929).
- ¹⁸ *Ber.*, **62**, 2906 (1929).
- ¹⁹ Pohle, *Kolloidchem. Beihefte*, **13-14**, 6 (1921); Klein and Stamberger, *Kolloid-Z.*, **35**, 362 (1924).
- ²⁰ Sheppard, *Nature*, March, 1921, 73; McBain, *Colloid Symposium Monograph*, **8** (1926); Sheppard and Houck, *J. Rheol.*, **1**, 20 (1929).
- ²¹ *Kolloid-Z.*, **49**, 140 (1929).
- ²² *Kautschuk*, **5**, 128 (1929).
- ²³ *Loc. cit.*
- ²⁴ *Nature*, July, 1929, p. 13.
- ²⁵ Stamberger, "Colloid Chemistry of Rubber," p. 54.
- ²⁶ *J. Am. Chem. Soc.*, **49**, 2230 (1927).
- ²⁷ *Kolloid-Z.*, *loc. cit.*
- ²⁸ *Nature*, June, 1928, p. 23; *J. physik. Chem.*, **33**, 371 (1929).
- ²⁹ *Nature*, July, 1928, p. 21; *J. Chem. Soc.*, 1928, 2791.
- ³⁰ *Naturwissenschaften*, **30**, 1513 (1928).
- ³¹ Stamberger, *Rec. trav. chim.*, **47**, 973 (1928).
- ³² *Ber.*, **62**, 2128 (1929).

Some Properties of Carbon Black

D. Parkinson

The term "*carbon black*" will be used in this paper to include all the varieties of moderately pure carbon existing in the form of soot. So far as the rubber industry is concerned, four distinct types of carbon black are in general use, as follows:

(1) *Gas Black*.—Sometimes itself called carbon black, made by the incomplete combustion of natural gas, the principal component of which is methane. The flames of burning gas impinge on metal surfaces, on which the black is deposited. (Cf. Neal and Perrott, Bull. No. 192, *United States Bureau of Mines*, 1922.)

(2) *Acetylene Black*.—Produced by the explosive combustion of purified acetylene in closed chambers.

(3) *Lamp Black*.—Obtained by incomplete combustion of fats, oils, tars, etc. Unlike the gas black particles, which are removed from the interior of the flame, those of lamp black pass through the outer layer before deposition. (Twiss, *India Rubber J.*, 65, 607, 651, 393 (1923)).

(4) *Thermatomic Black*.—Made by thermal decomposition of natural gas out of contact with air.

The difference in physical properties of these blacks depends largely on differences in heat treatment during manufacture. They are arranged above in order of the size of the individual particles, those of gas black easily averaging the smallest.

Particle Size.—Though gas black is the filler *par excellence* where great toughness and high resistance to abrasion are required in a rubber compound, only approximate information has yet been published as to its fineness. Particle size determinations of this substance are difficult because the particles, at all events the smaller of them, are of colloidal dimensions, and consequently below the limits of ordinary microscopic resolution. Green (*Chem. Met. Eng.*, 28, 63 (1923)), who has developed a microscopic method of determining the average diameter of small particles, states that gas black is one of the most difficult subjects for microscopy, and that it can be successfully photographed only with the use of ultra-violet light. He considers the average diameter to be about 0.15μ . One would expect this estimate to be somewhat high, since the most finely divided material cannot be seen.

The so-called obscuring power method was used by Vogt (*India Rubber World*, 65, 347 (1922)) to estimate the relative degrees of fineness of compounding ingredients, but it was later shown by Spear and Endres (*Ind. Eng. Chem.*, 15, 725 (1923)) that the method was not applicable in the case of particles which form colloidal systems. By Perrin's method of counting the particles in a dark field, Peterfi (for A. Wegelin, A. G., *Kautschuk*, 3, 196 (1927)) determined the average particle size of three samples of German carbon black as 124, 106, and 83μ , but pointed out that these values make no claim to mathematical exactitude. Barnard, in a communication to Wiegand (*India Rubber Journal*, 73, 31 (1927)), gave a figure of 50 to 60μ as the particle diameter of American gas black obtained by methods of filtration and counting in an ultra-violet microscope. Quite recently Grenquist (*Ind. Eng. Chem.*, 21, 667 (1929)) by ultra-microscopic examination has estimated that the diameter of individual particles of gas black ranges from 15 to 200μ .

None of these methods, however, gives any information regarding the distribution of particle sizes. What is the proportion, for instance, of particles greater than 100μ , or less than 50μ in diameter? This is not a question of mere theoretical interest, but is of practical importance to the rubber compounder. Investigations now proceeding on particle size distribution confirm the observations of Grenquist, on the upper limit of 200μ , and show a considerable proportion of the material to consist of particles smaller than 50μ in diameter.

Lamp black is a somewhat easier subject for analysis than gas black, since its particles are just large enough to give a true image in a good microscope. Green (*loc. cit.*) states that they are about 0.3 to 0.4μ in diameter. Distribution curves recently obtained support Green's conclusions. The optimum of the curve lies in the region of 0.3 to 0.6μ , but a fair proportion of particles occur in the region 0.6 to 1μ .

The average particle diameter of thermatomic black appears to be of the order of a micron. Detailed investigations have not yet been made by the writer on this substance. Under the microscope it appears coarser than lamp black (Goodwin and Park, *Ind. Eng. Chem.*, **20**, 621 and 706 (1928)).

So far as the writer is aware there is no published information regarding the state of subdivision of acetylene black. Research is now proceeding which shows it to be intermediate in fineness between gas black and lamp black. The larger particles are similar in size to those of lamp black, but a fair proportion of particles come within the gas black range. This can be strikingly demonstrated in a simple manner. Thus it is seen that there is a progressive change in color of light transmitted by very dilute suspensions of lamp black, acetylene black, and gas black, respectively, from a blue in the case of lamp black through a grayish color for acetylene black, to a bright amber in the case of gas black. The reasonable assumption—which if necessary could be supported by various lines of evidence—is that the differences in color are dependent largely on differences in particle size. If an uncentrifuged suspension of acetylene black be diluted it assumes the color characterized by acetylene black, whereas a centrifuged sample of the black assumes the amber tint characteristic of gas black. As the larger particles have been thrown out of suspension by centrifuging, the transmitted light possesses the color of a gas black dispersion, provided the particles are sufficiently small, and this is in fact the case. The effect can be produced with lamp black and even with thermatomic black, but is not so pronounced because of the small proportion of very fine material.

Attempts have been made to measure particle size by means of x-ray analysis, though it appears doubtful whether it will be possible to develop the method sufficiently to give more than approximate information. Goodwin and Park (*loc. cit.*) report an examination by Wykoff of five different samples ranging from a varnish black in a finer state of subdivision than rubber gas black, to a thermatomic black, in which a similar type of diffraction pattern was found for each black, but with a breadth of line following the estimated particle diameter.

It has been demonstrated by various workers that the strongest of all the so-called reinforcing agents added to rubber mixings is also the one in the finest state of subdivision, that is, gas black. This is probably a consequence of the fact that the smaller the particle the larger the ratio of surface to mass, and the larger the surface the greater is the boundary surface energy or interfacial tension between the filler and the rubber matrix. In addition to this, as the particles get smaller their intrinsic free energy becomes greater, owing to their high degree of curvature, a greater proportion of each molecule lying outside the surface, so that a greater proportion of its energy is available as free surface energy. The effect

of very small particles, therefore, is to increase the free energy not only by increasing the surface, but by increasing the energy per unit area of surface. It has been argued (Blake, *Ind. Eng. Chem.*, **20**, 1084 (1928)) that particle size should have nothing to do with the reinforcing power of a filler unless the character of the surface changes with particle size. But from the above considerations it is evident that a change in the character of the surface does occur with a change in the size of the particles, provided they are small enough to possess highly curved surfaces.

To say that a filler reinforces because its particles possess a large amount of free surface energy is no explanation at all, but the idea provides a basis from which, as knowledge progresses, it may be possible to build up satisfactory theories on what appears to be a complicated phenomenon.

The term *reinforcement* has been used by different writers in rather different ways. In the sense used by Wiegand (*India Rubber J.*, **70**, 503 (1925)) a good reinforcing filler may be defined as one which imparts to the vulcanized rubber a high tensile strength, along with a moderately high ultimate elongation, over a considerable range of volume loading. Such a definition takes account of energy absorbed by the rubber when stretched to rupture over a series of filler concentrations. This energy input has been denoted by such terms as "resilient energy capacity" and "proof resilience," but the term "energy absorption" recently used by Dawson (*Trans. Inst. Rubber Ind.*, **5**, 48 (1929)) would appear to be more appropriate. Wiegand's ΔA function (*loc. cit.*), which is the integral of excess energy absorption supplied by the filler over that of the base mix, with respect to volume loading, provides a convenient means of representation of reinforcing effect. Judged from this standpoint, gas black occupies first place as a reinforcing agent.

From the small amount of published information it would appear probable that acetylene black approaches gas black very nearly in reinforcing effect. This might be expected from its near approach in particle size. Investigations by Dawson (*loc. cit.*) show that up to 25 per cent. by weight of black in a 95-rubber-5-sulfur stock the energy absorption curves for the two blacks may be regarded as identical. It would be interesting to see further comparisons with greater concentrations of filler. The energy absorption was shown to be lower in the case of lamp black, a result in accordance with its larger particle size.

Lunn (*Trans. Inst. Rubber Ind.*, **4**, 396 (1929)), also considering reinforcement in terms of energy, but attacking the problem from a new angle, found that gas black showed a reinforcing effect far superior to that of thermatomic carbon, the latter substance more nearly resembling zinc oxide. Acetylene black and lamp black were not included in the investigations. Cranor (*India Rubber J.*, **70**, 63 (1925)) had previously shown that the stress-strain curves of rubber compounded with zinc oxide and thermatomic black were closely similar.

A survey, which makes no claim to be exhaustive, of the literature indicates that properties like energy absorption, tensile strength, and abrasion resistance are, with rare exceptions (Goodwin and Park, *loc. cit.*), increased to a greater extent by the addition of gas black than by any other filler. Acetylene black probably occupies second place and lamp black third.

Within the range of lamp black to gas black it would appear that there is no close relationship between modulus and degree of fineness of the filler. The stiffening effect appears to vary according to the accelerator used, the influence of the latter often masking that due to particle size differences. Thermatomic black, however, invariably gives a low modulus.

A property of rubber which appears to vary in accordance with the particle size of the added fillers is that of resilience, which is a measure of the energy returned after the rubber has been submitted to a low deformation.

Resilience, to quote Healey (*Rubber Age (London)*, 5, 621 (1925); *India Rubber J.*, 69, 57 (1925)), "is the opposite of hysteresis and measured under different conditions of time." Healey has kindly allowed the writer to reproduce some curves, showing the effects produced on resilience and hardness of rubber by the addition of increasing volumes of gas black, lamp black, and acetylene black. The experiments were carried out by C. D. Law in 1923 on an instrument of the pendulum type designed by Healey. "The resilience (again quoting Healey, *loc. cit.*) is determined by measuring the rebound of a pendulum after striking a rigidly fixed block of rubber, and the hardness or stiffness is calculated from observations of velocity of impact and amount of distortion of the block."

The black was added to a base mixing containing rubber 93, sulfur 5, and magnesia 1. The curves (see Figs. 1, 2, 3) show that gas black at all concentrations gives the lowest resilience. At low concentrations lamp black and acetylene black are about equal but better than gas black, but at higher volume loadings lamp

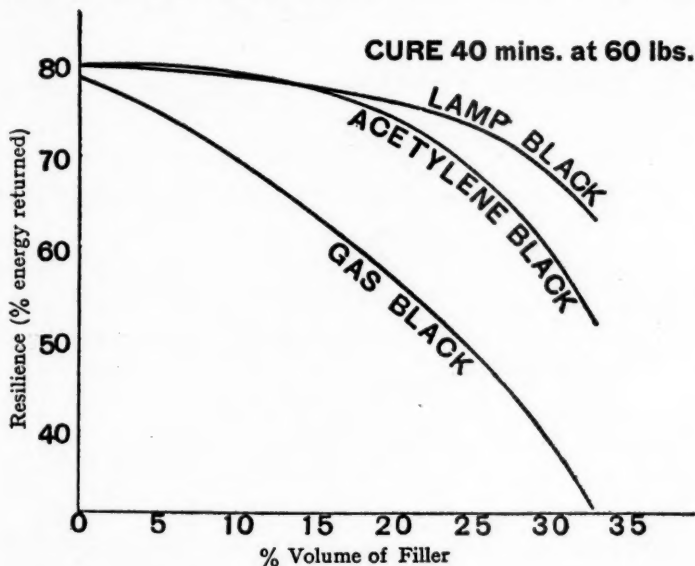
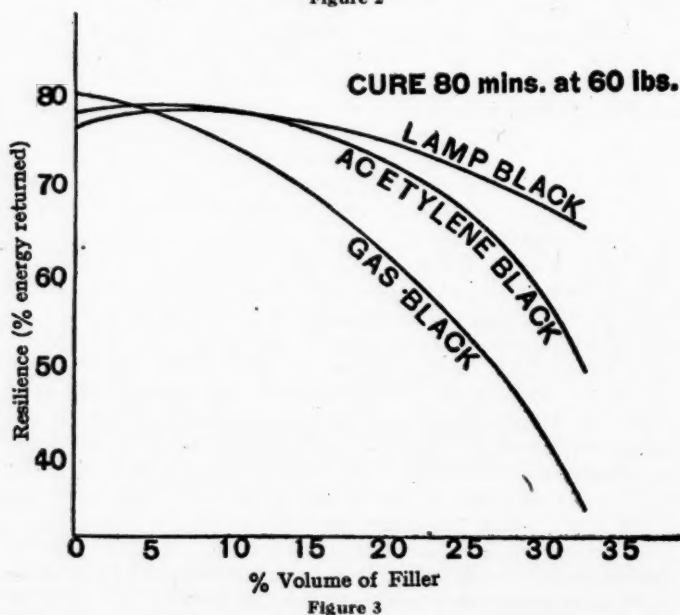
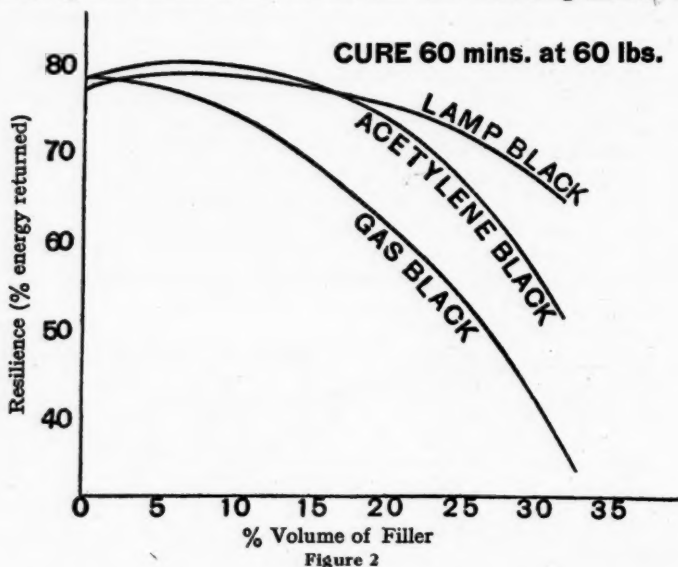


Figure 1

black gives a higher resilience than acetylene black. These results are in order of the particle size of the blacks, and it would appear that this is partly due to increased friction during deformation between the rubber matrix and the filler with increased development of interface. But if this were the complete explanation we should expect the resilience always to decrease with increased filler concentration. This actually happens with gas black, but the lamp black and acetylene black curves show that the resilience does not fall appreciably until about 15 volumes of filler are added. Indeed Healey has shown (*loc. cit.*) that zinc oxide and magnesium carbonate up to relatively large concentrations increase the resilience. The hardness curves, on the other hand (see Figs. 4, 5, 6), appear to show little relation to particle size within the range of the three blacks; if anything, acetylene black gives a harder mix. The gas black stocks are somewhat soft at the low cure, probably due to a retardation of the cure by the black.

On the other hand, the researches of Goodwin and Park (*loc. cit.*) indicate that,

over a range of five different types of black, hardness, whether measured by dynamical (pendulum) or static methods, increases with decreasing particle size. These investigators attribute this to the fact that increasing fineness increases



the total surface of a given mass of filler. On the other hand, they adduce evidence to show that tensile strength, modulus, energy absorption, and abrasion resistance do not invariably arrange themselves in order of fineness of the filler.

Particle Shape and Structure.—Magnesium carbonate is an example of a compounding ingredient which reinforces more strongly than gas black at low concentrations (Greider, *Ind. Eng. Chem.*, 15, 504 (1923)). Wiegand (*loc. cit.*) has argued reasonably that this is to be expected because, as the particles depart markedly from sphericity, there is a more rapidly increasing superficial area of contact between rubber and filler phase than in the case of approximately spherical particles. At higher concentrations the reinforcing effect falls off rapidly because, according to Wiegand, of agglomeration of the particles. There seems to be a tendency for elongated particles generally to agglomerate more readily than particles which approximate to spheres. But even if such particles as those of magnesium carbonate or china clay (which contains mica flakes in some abundance) were perfectly dispersed, we should not expect them to develop so much surface

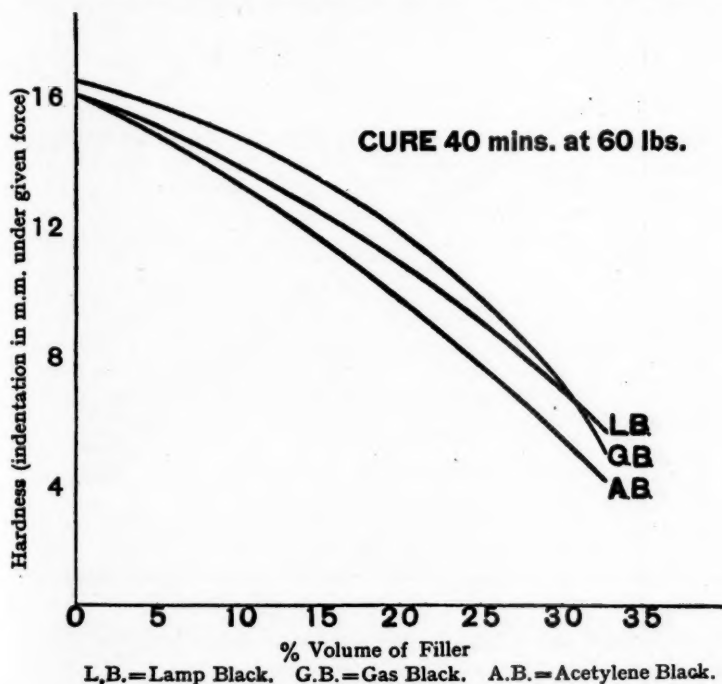


Figure 4

energy as spherical particles owing to the high degree of curvature of the latter. No comment is needed on the grain effects produced by elongated particles (Vogt and Evans, *Ind. Eng. Chem.*, 15, 1015 (1923); Endres, *Rubber Age (London)*, 5, 578 (1925); Schidrowitz, *Trans. Inst. Rubber Ind.*, 2, 89 (1926-27)).

It is not known how far carbon black particles depart from the spherical. In this and other respects a knowledge of the ultimate structure of the particle is of importance, though inadequate in itself to indicate the actual shape of the particle. It is not known with certainty whether the so-called amorphous carbon (including charcoal and the varieties of carbon black) is truly amorphous (*i. e.*, its molecules are arranged in a haphazard or disorderly manner) or crystalline on a very minute scale. Debye and Scherrer (*Phys. Z.*, 18, 291 (1917)) conclude from x-ray analysis

that there is no essential difference between amorphous carbon and graphite (which crystallizes in the hexagonal system), the amorphous varieties being merely in a finer state of subdivision. Asahara (*Chem. Abstr.*, 17, 656 (1923)) arrived at similar conclusions, and states that carbons produced by the decomposition of certain gases or vapors such as carbon monoxide, acetylene, carbon disulfide, and coal gas, show no sign of definite crystalline form, but give definite interference figures which seem to establish their crystalline nature. Some indirect support is given to these views by the researches of Lowry and Morgan (*J. Phys. Chem.*, 29, 1105 (1925)), who have succeeded in preparing finely divided graphite with an adsorptive capacity about one-third that of charcoal. (Graphite in the ordinary state is non-adsorptive.) Pickles (*Trans. Inst. Rubber Ind.*, 2, 85(1926-27)) reports work carried out by the Radiological Dept. at Woolwich Arsenal, in which

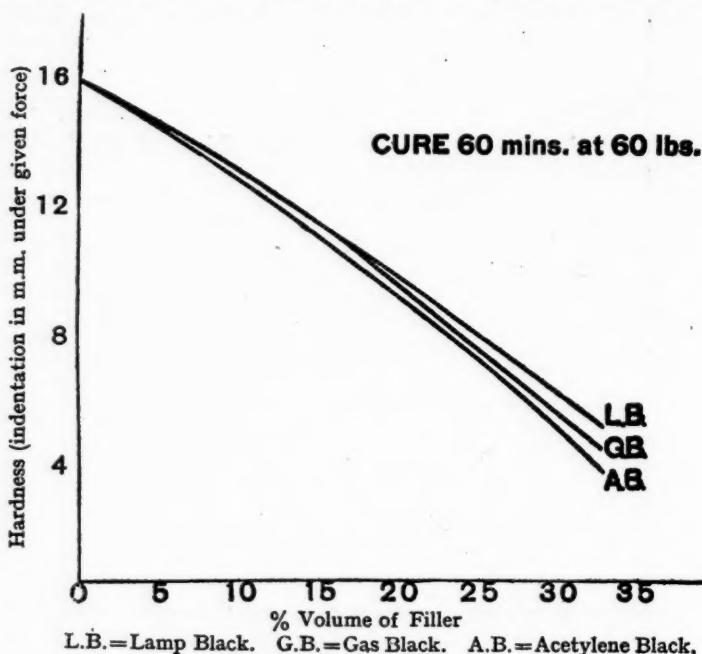


Figure 5

"it was found that acetylene black, American gas black, and oil black all exhibit much the same spectroscopic characters, and that they probably all consist of mixtures of the crystalline and amorphous varieties of carbon, although the percentage of crystalline structure is greater in the acetylene black than in the others." Clark (*Ind. Eng. Chem.*, 18, 1131 (1926)) considers that x-ray patterns show a continuous change from a practically amorphous state to a crystalline graphitic state, according to the particle size of the black. Goodwin and Park (*loc. cit.*) consider that all the blacks they examined are probably in some degree crystalline, but state the possibility that they may contain a mixture of crystalline and amorphous carbon, with enclosed hydrocarbon. More or less similar views have recently been expressed by Grenquist (*loc. cit.*).

On the other hand, Raman (*Nature*, 123, 945 (1929)) has recently stated that

"careful studies by Krishnamurti of the x-ray patterns of sugar charcoal and lamp black prove conclusively that these substances do not possess any crystalline structure." Considerable weight must be attached to this very emphatic statement by so high an authority, and the publication of the research referred to will be awaited with interest.

But whether the particles are crystalline or amorphous, x-ray analysis can tell nothing about their actual shape. The geometrical form of a crystal is not necessarily related to its crystalline form, the latter being an inherent property of the material, and dependent on the arrangements assumed by the molecules themselves—the so-called space lattice of the crystal; whereas the external shape, though influenced by the internal pattern and spacing, depends more on the conditions under which the crystal grows. Thus it is possible for a crystal in the cubic (or regular) system to assume an elongated form, because it is free to grow more in one direction than in any other. Such a crystal particle a rubber technologist would term anisotropic, whereas in the optical sense it is isotropic, since light travels through it with the same velocity in all directions. On the other hand, optically anisotropic crystals, though usually elongated or flattened due to unequal lengths of axes, may be sufficiently nearly equidimensional to be termed isotropic in the geometrical sense.

Spear has suggested (*India Rubber World*, 71, 18 (1924-25)), in discussing the character of the surface of the gas black particle, that "It seems probable that the surface of the most valuable types of carbon black may resemble a burr rather than a marble. In other words, the particles are deeply serrated, so that the actual surface is very much larger than the diameter measurements would indicate." There is no evidence whatever, so far as the writer is aware, in support of this hypothesis. Though such a colloid particle might possibly exist, it seems unlikely that any of the known methods of determining particle shape would be capable of detecting it. These methods can do no more than indicate (1) whether the particles are approximately spherical or elongated and (2) if elongated whether they are rod-like or disc-like.

In this respect little experimental work appears to have been carried out on carbon blacks. Goodwin and Park (*loc. cit.*) note the twinkling effect which elongated particles give when in Brownian motion with various samples of black, and state also that anisotropy is indicated in rubber-black mixes cut with and across the calender grain. Grenquist (*loc. cit.*), using an ultramicroscope with an azimuth stop, observes that gas black "suspensions contained both isotropic and anisotropic particles, the anisotropic having a much greater tendency to aggregate than the isotropic."

It is hoped that an apparatus which has just been constructed may throw further light on this problem.

Degree of Blackness.—The amount of light absorbed by different carbon blacks appears to be related to their fineness of division. Thus the degree of blackness increases in the order thermatomic black, lamp black, acetylene black, rubber gas black, varnish gas black (super spectra), *i. e.*, with decreasing particle size. The grayness of thermatomic, the blackness of gas black, and the intermediate position occupied by lamp black are obvious from ordinary inspection. Smaller differences in light reflection from black powders can be detected photometrically by means of an instrument called the nigrometer (Johnson, *India Rubber World*, 77, 65 (1928)).

Adsorptive Capacity.—This is a property which is possessed in varying degrees by amorphous carbon. The extent of adsorption will depend on the ratio of surface to mass of the adsorbent and on the character and intensity of the free

energy of the adsorbed molecule. There may be other factors involved, but these need not be considered. Gas black particles are covered with a film of adsorbed air which can be removed by heating the powder in a vacuum, or by displacement by a liquid possessing a high wetting power. Carbon black is not wetted by water partly because the wetting power of the water is not high enough to remove the adsorbed layer of gas.

Preliminary experiments by the writer on adsorption of gases indicate that the degree of adsorption by carbon blacks is, as would be expected, a function of their specific surface, those with the smallest particle size adsorbing the most gas. Goodwin and Park (*loc. cit.*) found that the adsorptive capacity of carbon blacks, both for iodine and methylene blue, followed the order of particle size, while the moisture content, which ought to depend on the adsorptive power, followed the

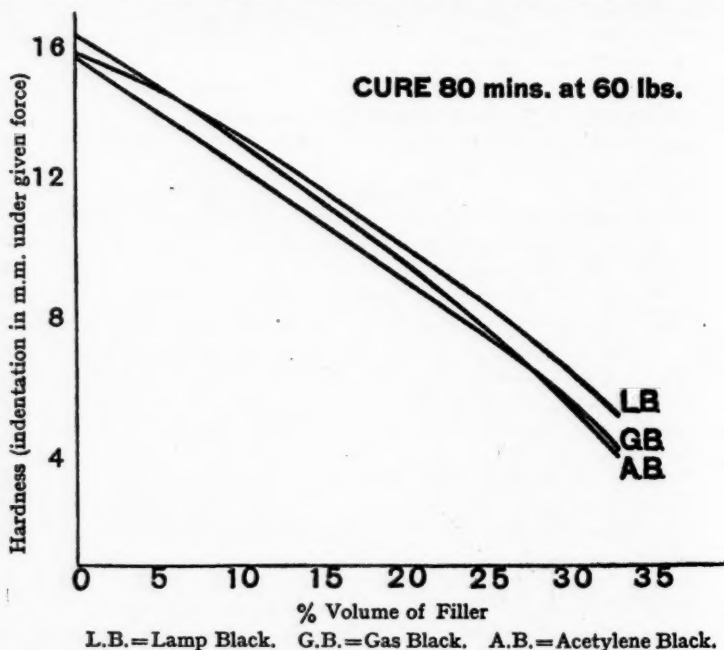


Figure 6

same order. Quite recently Carson and Sebrell (*Ind. Eng. Chem.*, **21**, 911 (1929), and *Rubber Age (London)*, **10**, 305 (1929)) have obtained results for iodine adsorption in essential agreement with those of Goodwin and Park. Carson and Sebrell also give results of experiments showing that the accelerators diphenylguanidine and mercaptobenzothiazole are adsorbed by carbon blacks in amounts which bear some relation to the particle size of the blacks. They also give evidence of adsorption of sulfur by gas black. Beaver and Keller (*Ind. Eng. Chem.*, **20**, 817 (1928)) have also compared the iodine adsorptive capacities of various blacks, the order of decreasing adsorption being ink black, rubber gas black, acetylene black, lamp black, and thermatomic black.

Adsorptive capacity, and hence to some extent particle size, seems to be closely related to rate of vulcanization. Twiss and Murphy (*J. Soc. Chem. Ind.*, **45**, 121T (1926)) showed that gas black in unaccelerated mixings exerts a marked retarding

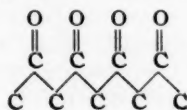
effect on the rate of cure, and attribute this property to adsorption of part of the natural accelerator in the rubber by the black. Goodwin and Park (*loc. cit.*) consider that adsorptive capacity exerts a profound influence upon the character of a rubber mix, especially in its tendency to retard the rate of cure. Carson and Sebrell (*loc. cit.*) also find the rate of vulcanization to be a function of adsorptive capacity; but Beaver and Keller (*loc. cit.*) find no relation between adsorption and rate of cure. It seems possible that in the latter case the influence of the accelerator (Grasselerator 808) may have masked to some extent the retarding effect on the cure by the different blacks.

It is considered by some investigators that rubber itself is adsorbed by carbon black; in other words, that the bond presumed to exist between rubber and filler is in the nature of an adsorptive attachment. Stamberger (*Kolloid-Z.*, **42**, 295 (1927)), from a study of sedimentation and diffusion in rubber-filler cements, has produced some evidence in favor of the view that a portion of the rubber is adsorbed by the filler. He is of the opinion that the property of carbon black of stiffening over-masticated rubber can be explained on the basis of adsorption. By a mechanical addition, the gel structure, which has been destroyed by mastication, is restored.

Volatile Components and Adsorbed Gases.—Hulett and Cude, in coöperation with Neal and Perrott (*loc. cit.*), determined the nature of the gases pumped off from four samples of ink black at room temperature and at 445° C. At the lower temperature the composition of the gases obtained was approximately that of air, which we may assume was present as an adsorbed layer, but at 445° C. a larger volume usually came off, consisting chiefly of carbon dioxide and carbon monoxide, with small amounts of other gases. This may not have consisted entirely of adsorbed gas. It is stated that before heating, oxygen was probably present as fixed oxygen, that is, in some form of combination with the carbon.

Ultimate analyses show that carbon blacks contain oxygen in varying amounts up to more than 10 per cent. A gas black produced for use in rubber usually contains between 5 and 6 per cent. oxygen, 1 per cent. hydrogen, and traces of nitrogen and sulfur. Analyses, however, give little information concerning the original chemical condition of the components. For this reason Johnson (*Ind. Eng. Chem.*, **20**, 904 (1928)) undertook a comprehensive study of the quantities and nature of the gases evolved at temperatures up to 955° C. from a series of blacks differing markedly in oxygen content. Carbon monoxide, carbon dioxide, and hydrogen were obtained in large quantities, and Johnson gives evidence strongly indicating that the oxides of carbon are reaction products. He makes the interesting suggestion that Langmuir's conception of a surface union of oxygen to the carbon filament of an electric lamp may possibly be applied to account for the oxygen in carbon black.

Langmuir calculates (*J. Am. Chem. Soc.*, **37**, 1139 (1915)) that if it is assumed that molecules of oxygen are placed in a single layer on a surface, much as the cells in honeycomb are arranged, the total number required to cover a sq. cm. is 1.6×10^{15} . From considerations of the atomic structure of solid bodies Langmuir argues that the carbon atoms in the filament must be considered as forming endless chains with each other. He considers the oxygen atom to be chemically combined with one of the outer carbon atoms in a structure represented below.



Applying this principle to gas black it is easy to show, making the reasonable assumption that the particles are spheres of average diameter, 50μ , that a monomolecular layer of oxygen combined with the surface atoms in one gram of black will weigh 0.055 gram. In other words, on the assumption of the truth of this theory standard rubber gas blacks ought to contain about 5.5 per cent. by weight of oxygen.

A sample of this type of black quoted by Neal and Perrott contains 5.06 per cent. of oxygen. Beaver and Keller (*loc. cit.*) used a rubber gas black containing 5.3 per cent. oxygen. Johnson quotes three samples of black all produced by the channel process for use in rubber, which contain, respectively, 3.89, 4.15, and 6.73 per cent. of oxygen. One is tempted to suggest that these samples might vary in particle size, but whether this is the case or not, agreement with the theory is good. Some ink blacks contain more oxygen than rubber gas blacks, and these are probably smaller in particle size. A sample of acetylene black used by Beaver and Keller contained 2.6 per cent. oxygen, a value in keeping with the larger particle size of the black.

The monomolecular layer theory, however, fails to hold in the case of lamp blacks, which contain oxygen in similar or larger amounts than gas black.

An effect of heating carbon black and amorphous carbon to very high temperature under low pressure is to destroy the adsorptive power of the carbon. Lemon (*Phys. Rev.*, **14**, 281 (1919)) showed that the adsorptive capacity of cocoanut charcoal is greatly reduced by evacuation at 900°C . and completely destroyed at 1200°C . With some charcoals a still higher temperature than this is required to render the material non-adsorptive (Howard and Hulett, *J. Phys. Chem.*, **1924**, 1082). Johnson (*loc. cit.*) found that once the volatile matter is driven off at 955°C . carbon blacks largely lose their capacity to adsorb gas, as is indicated by their no longer possessing any appreciable hygroscopic property.

Carson and Sebrell (*loc. cit.*), however, show that heating gas black to 900 – 1000°C . actually increases the adsorptive capacity for iodine, and attribute this to the removal of adsorbed material. It seems possible, though, that if the heating had been carried out at low pressure the results might have been different.

Johnson (*loc. cit.*) shows that blacks containing a high percentage of volatile matter considerably retard the rate of vulcanization, while Beaver and Keller (*loc. cit.*) come to the conclusion that the presence of oxygen in carbon retards the rate of curing, and also increases the rate of aging of the rubber.

Dispersion of Carbon Black in Rubber.—The dispersion of very small particles such as those of gas black in rubber is essentially a colloidal phenomenon. A complete dispersion is one in which every particle is separated from every other particle in the dispersion medium, in this case the rubber. Such a condition approximates to the ideal in compounding, and is probably never completely attained, except possibly with a very small concentration of filler.

The obvious way to test whether a filler is well or poorly dispersed in rubber is to examine thin sections microscopically. Grenquist (*Ind. Eng. Chem.*, **20**, 1073 (1928); **21**, 665 (1929)) has studied rubber-gas black mixings microscopically both before and after vulcanization, and also throughout the vulcanization process by means of a steam-heated micropress developed by Hauser and Hünemörder (*India Rubber World*, **79**, 59 (1928)). He observes that during mixing the particles tend to aggregate round any larger nucleus present in the rubber while during vulcanization flocculation occurs because of the increased mobility of the rubber. The black particles have the effect of inhibiting the formation of crystals from the free sulfur. This, in Grenquist's opinion, is "partly due to their adsorptive capacity toward sulfur, and partly because they fill up the rubber matrix, forming

a close network, which prevents the formation of large sulfur crystals in the rubber."

The microscopic method, valuable though it is, fails, however, to provide a quantitative measure of dispersion. Attempts in this direction by means of x-ray analysis have so far met with little success in distinguishing between well and ill dispersed compounds. Grenquist (*loc. cit.*) found by x-ray photographs taken with various types of black dispersed in rubber in a concentration of 30 per cent. that practically identical patterns were obtained in all cases, probably due, according to the author, to a superimposing of rubber and filler patterns.

A calorimetric method which gives indications of degree of dispersion has been developed by Hock and his co-workers (*India Rubber J.*, **74**, 419, 453 (1927)). These investigators, by indirectly estimating the heat of adhesion between rubber and filler from consideration of the heat of swelling of rubber in a solvent and the heat of wetting of the filler in the same liquid, have derived information concerning the boundary surface energy between rubber and filler. Results so far obtained indicate that the heat of adhesion per unit mass of filler progressively diminishes as the compound becomes richer in filler. In terms of dispersion this simply means that as concentration increases, the percentage amount of filler dispersed decreases, because a decreasing percentage of the surface of the filler forms a common boundary with the rubber.

This explains partly why the maximum reinforcing effect of a filler is always reached at a relatively low concentration, since we should not expect undispersed particles to show appreciable reinforcement. Under present compounding methods there seems to be an early limit to the volume of filler which can be dispersed in the rubber. This varies for different fillers, but is always very far below the theoretical limits computed from a consideration of different systems of piling of solid particles.

It is not known why it is not possible to disperse more than a certain amount of filler, or why some fillers disperse better than others, but a connection can be traced between dispersion and ease of wetting of the filler by the rubber. This, again, is a phase of the problem about which little appears to be known. The state of aggregation of the particles in the powder before incorporation and the existence and nature of electric charges are probably among the factors involved. It has been stated (Endres, *Rubber Age*, **5**, 578 (1925)) that the layer of adsorbed gases surrounding the particles assists in dispersion because it prevents the particles from coming within their spheres of adhesion. But if this were so we should expect varnish blacks (*supra spectra*), which contain more adsorbed gas than rubber gas blacks, to disperse more easily than the latter, but the reverse seems to hold (Goodwin and Park, *loc. cit.*). It must be remembered also, that for complete wetting the adsorbed layer has to be removed, and this must have the effect of making wetting more difficult.

A consideration of wetting involves the idea of a surface angle of contact. Where wetting is perfect this angle approximates to zero, and the reduction in surface tension is a maximum. With fillers of very small particle size the angle of contact with the rubber matrix, if not zero, is probably not far from it, but it is not known whether it varies with fillers of like particle size and shape.

So far as present knowledge is concerned there is no *proof* that the reinforcing effect of chemically inert compounding ingredients depends on factors other than those which can be attributed to particle size, shape, and degree and extent of dispersion of the particles. Statements sometimes appear to the effect that particle size in rubber is not necessarily the same as in other media. It seems to the writer that this is not a particularly good way of expressing the facts. If space permitted several lines of evidence could be adduced to show that the particle size of a ma-

terial like gas black, which is produced by a condensation process as distinct from one of disintegration, is a specific property of the material. The particles can exist in two states, either as separate individuals or as agglomerates. In the case of flocculates, as the term is understood by rubber technologists, the particles are bunched together, though completely separated from each other, more or less like star clusters in the galaxy. If then, dispersion is complete, the fineness of division will be that of the individual particles.

From these considerations it seems evident that any method of improving the dispersion of a filler should increase the strengthening properties of the filler. Certain softeners, such as stearic acid, have been claimed to possess the property of assisting dispersion. In fact, Blake (*Ind. Eng. Chem.*, 20, 1084 (1928), and 21, 218 (1929)) goes so far as to assume that it is the natural fatty acids, mainly stearic, in the rubber, along with any acid which may be added, that are the true dispersing agents, and not the rubber itself. By applying the principles of Langmuir's work on monomolecular films of fatty acids on water to the rubber-filler problem, Blake shows, from a consideration of the particle size of the gas black, and the cross sectional diameter of the stearic acid molecule, that the amount of fatty acid naturally occurring in the rubber is just about sufficient to form an adsorbed monomolecular film round each particle of gas black when the latter is compounded to an extent of 30 volumes to 100 volumes of rubber. It is assumed that the average diameter of the gas black particle is 0.2μ , a value which is much too high, and the black, if fully dispersed, develops three or even four times the surface assumed by Blake, and hence three or four times the amount of fatty acid occurring in the rubber would be needed fully to disperse the black. But apart from this, if the theory be true it ought to be either impossible or very difficult to disperse gas black in rubber from which the fatty acids have been removed.

To test this, two mixings were made containing rubber 100, gas black 50 parts by weight, acetone-extracted rubber being used in one of them. The black mixed quite readily in the acetone-extracted rubber, and appeared from microscopic examination to be quite as well dispersed as that mixed in the unextracted rubber. Dilute solutions in xylene of the two mixings gave the amber tint characteristic of good dispersion.

Attempts were also made, under varying experimental conditions, to disperse gas black in solutions of stearic acid, but these were unsuccessful. It would appear, therefore, that stearic acid has little, if any, influence on the dispersion of gas black in rubber. From other considerations Depew (*Rubber Age (New York)*, 24, 378 (1929)) and Goodwin and Park (*loc. cit.*) have come to a similar conclusion.

The author wishes to express his thanks to Messrs. Healey and Law for allowing him to make use of the results of some of their work on hardness and resilience of rubber, to Mr. B. Martin for assistance, and to the technical manager of the Dunlop Rubber Co., Mr. A. Healey, for permission to publish results of research carried out in the laboratories of the Company.

The Testing of Automotive Rubber Parts Assembled under Compression¹

Part I—Deflection under Compression

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Present-day test specifications on automotive rubber parts are not only incomplete and misleading, but entirely lacking in uniformity. This is particularly true of compression and permanent-set tests on automotive mechanical rubber parts assembled under compression. Consequently, an effort has been made to show the urgent need for unification of such methods.

Data are presented in Part I to show that high tensile is no criterion of relative resistance to compression set and that hardness is not a measure of deflectability. In addition, deflection and permanent set under compression are greatly influenced by the size and shape of the test piece, the method of cutting the sample, the gage and methods of measuring it, and condition and kinds of surfaces in contact with the test piece.

Compression and compression-set testing equipment are discussed, and some newly designed laboratory equipment is described. One piece of apparatus, the compression-set meter, has been found extremely useful in making deflection, hysteresis, and set tests. These tests may be performed under constant load or constant distortion. The constant-load (spring) compression-set clamp is suggested as a suitable laboratory standard for permanent-set testing under compressive loads.

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IN KEEPING with the rapid strides in the automobile industry, an almost endless variety of rubber mechanical goods is being used in motor car manufacture. As a result there has arisen a great variety of tests and test specifications, many of which are worthless for evaluating the parts under consideration. In fact, some of these specifications, particularly those requiring compression- and permanent-set tests, are often defeating the purpose for which they were written. The authors of these specifications have either presupposed a uniformity in testing equipment and details of tests, and hence have very briefly stated the tests, or else, through a lack of appreciation of the many factors influencing the results, have failed to include such important details as

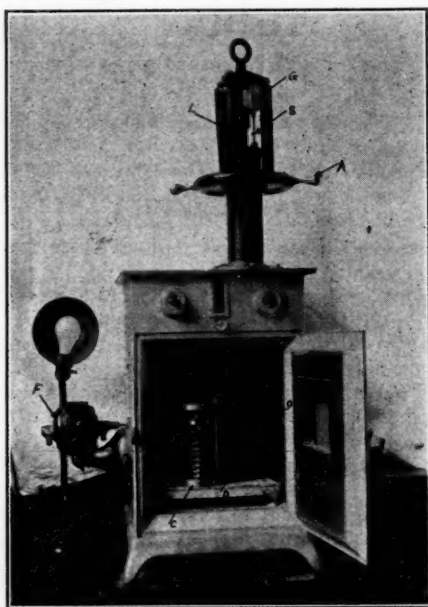


Figure 1—Compressetometer

size of test piece, gage, etc. Consequently many inferior stocks may pass these specifications if the testing conditions are carefully chosen. There are generally other requirements, such as tensile, elongation, etc., to preclude the possibility of passing certain very low grade stocks, but even these requirements do not offer an absolute safeguard against inferior quality, for a very high tensile, for example, does not necessarily mean high quality in a good motor-support or shock-insulator stock. Undoubtedly modulus, stress, and elongation at break, and also percentage change in physical properties after aging are important in evaluating many rubber parts, and would be to a certain extent for automobile

mechanical goods also, were it not practically impossible to perform many of these tests on the rubber parts themselves owing to their peculiar shape and size. In many cases it may prove necessary to have the producer furnish with each shipment laboratory test slabs of the same stock for tensile, deflection, and set tests. In general, these test pieces will be given that cure which produces the maximum desired physical property rather than one identical with that of the part in question. This procedure makes it possible for an unethical producer to furnish samples of stock apparently identical in composition, yet of far better physical properties than those possessed by the parts included in the shipment. The question of equivalent cure is also very important and "mechanicals" will often necessarily differ greatly in cure from such test slabs.

To date it has been impossible to establish any true mathematical relationship between the results of tensile tests and those of many of the other mechanical tests. Goodwin and Park (4) have shown that the abrasion resistance of a tread compound cannot be judged merely by its tensile data. Likewise the writer (1) has shown that the data of tensile tests will not serve to evaluate properly the resistance of a stock to flexure under compression. In view of the above facts, it seems advisable to perform such tests as simulate, partly at least, service conditions.

Probably one of the most important groups of automobile mechanical rubber goods is that including parts assembled under compression, such as bumpers, engine and radiator pads, shims, shock insulators, torque insulators, etc. Nevertheless, most investigators appear to have almost wholly disregarded compression testing, particularly hysteresis and permanent set under compressive loads. Recently, however, Birkitt and Drakeley (3) have published some very interesting results of work on compression testing. Their data show that gage, area of test piece, and slippage all influence compression results, but apparently the results reported have only slightly, if at all, affected compression and permanent-set testing methods. Their tests were conducted at unusually high pressures per unit area. Ariano (2) also has experimented with molded cylinders of vulcanized rubber compressed in the direction of the axis between parallel plates. The apparatus could compress the cylinders to 45 per cent of their original height. His paper consists of a somewhat mathematical discussion of the form of the compression curve and some factors influencing it, but does not give details concerning laboratory procedure. Neither of these papers, however, attempts to correlate the factors studied with permanent set under compression.

Hippensteel (5) recently described a rubber compression-testing machine, which is capable of tests at considerably higher loads than are necessary for ordinary laboratory tests.

Early in the study of automotive rubber parts used to ab-

sorb vibration, the author was confronted with the necessity for a suitable device for conducting laboratory tests under compression, either at constant load or constant deflection, in order to compare resistance to flexure under compression with permanent set under compressive loads. Such a device (Figure 1) was then designed, as a co-testing device with the compression flexometer (1). The latter may be described as a dynamic flexure-compression testing device, while the new instrument, called a "compressetometer" may be considered as a static compression testing device inasmuch as permanent set and fatigue tests are performed under steady loads. The compressetometer is suitable for tests at loads up to 228 kg. (500 lbs.), which is a reasonable laboratory range. The capacity may be increased by substituting heavier springs. This device is much less expensive than the machine discussed by Hippensteel and furthermore makes possible many special tests, particularly tests at high and low temperatures.

Description of Compressetometer

The compressetometer, which is mounted in an electric oven, produces compressive loads on test pieces by means of

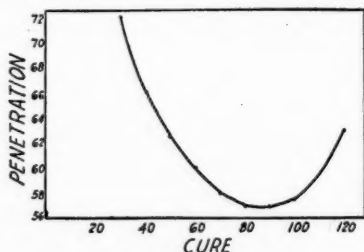


Figure 2—Hardness vs. Cure

three tension springs, placed outside the oven in order to avoid heat effects as much as possible. By turning the hand wheel, *A*, in a clockwise direction, the springs are made to pull a plunger, *B*, down onto a sample resting on the bottom plate, *D*. Loads are measured in 5-lb. units on the scale, *L*. The gage, *G*, measures deflections in thousandths of an inch. The spindle, *S*, can be adjusted to various heights to get the correct zero point on the deflection gage for various thicknesses of test pieces. A high degree of accuracy is possible, especially when testing small round disks cut from slabs, merely by lowering the plunger and noting the position at which it just touches the test piece. More positive accuracy is obtained, however, by first running the plunger down as far as it will go, setting the deflection gage to that reading corresponding to the thickness of the sample to be tested, and then raising the plunger and inserting the sample. The latter method is used in all research and special or comparison tests. A fan, *F*, provides circulation of air. A thermometer is so inserted through the orifice, *O*, that readings can be

taken through the glass in the door. As a special precaution in some cases, particularly in getting heat tests started, the thermometer is inserted from the front so that its bulb rests on the plate, *D*. In order to avoid errors due to temperature effects when standard permanent-set tests are made, it is necessary to insert the test piece between metal plates (at room temperature) with surfaces similar to those in the permanent-set equipment used. These are then placed in the compressetometer, which is already at the test temperature, and the required load is imposed on the test piece.

The majority of compression tests in this laboratory have been performed with the above equipment. Although the compressetometer is relatively easy to operate at loads up to 500 lbs., plans have been made to motorize this equipment for tests at higher loads. The instrument is also to be autographic so that complete hysteresis curves will be obtainable.

Method of Testing

In conducting compression and hysteresis tests, the loading and unloading are performed at the same arbitrarily fixed rates. In general, during the first half of the loading cycle, distortions are read at every 11.5 kg. (25 lbs.) or less, depending upon the size of the test piece, and finally at every 23 kg. (50 lbs.) as the slope of the curve becomes steeper (as $\Delta y/\Delta x$ increases). For unloading data, readings are taken at each of the distortions recorded during loading.

TESTS AT CONSTANT LOAD—In performing permanent-set tests at constant loads, the test piece is put into the compressetometer under the proper temperature conditions and compressed to the required load. There is an immediate fatigue effect, as shown by a change in the distortion during the first few minutes after the maximum load is reached. The rate of this change decreases rapidly, and this means a change in load. Consequently, for the first few minutes, and much less frequently for the next 3 or 4 hours, or even during most of the test, the hand wheel is so regulated that the load is kept constant. The drop in load over a 24-hour period due to fatigue of the samples is very small, particularly when the gage is approximately 0.635 cm. (0.250 in.) (normal or average gage for most set tests), so that continued load adjustments are unnecessary except in the most exacting tests. A change of 0.25 cm. (0.1 in.) or 40 per cent based on 0.635-cm. (0.250-in.) gage, in the position of the plunger causes a variation in the load of only approximately 3.18 kg. (7 lbs.) and no high-grade stock of this gage will show a distortion fatigue of 40 per cent in a 24-hour test at 70° C. at ordinary test loads. The error due to neglecting the actual fatigue effect is low, but depends on the load-deflection ratio of the spring used.

TESTS AT CONSTANT DISTORTION—If tests are to be run at constant distortion, the hand wheel must be run back to much lower loads than the initial maximum. Consequently,

frequent adjustments are necessary, particularly at first. The fatigue effect may result in a 50 per cent drop in the load in these distortion tests.

CHECK CALIBRATIONS—The compressetometer is also used to check calibrations of the springs used in compression-set clamps (Figure 1, C). The base, *D*, is removed and another base containing a well to receive the spring is substituted. The compressetometer itself is calibrated by means of dead weights hung from the ring shown at the top after inverting the instrument. The instrument is first removed from the oven and suspended by a hook screwed into the base, *D*.

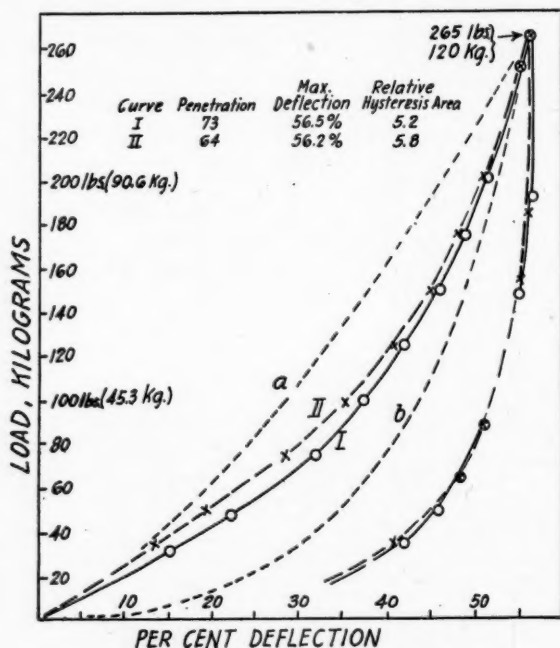


Figure 3—Load Deflection Curves of Two Disks of Penetration 73 and 64, Respectively

Relation of Hardness to Deflection under Compressive Loads

Hardness has been one of the most frequently discussed tests to be applied to mechanical goods. In the past no universally adopted instrument of any reasonable accuracy has been available to the trade. As commonly used, the term "hardness" refers to the resistance of the surface and adjoining layers of the rubber to a relatively small penetrating point of definite size when subjected to an arbitrarily determined load obtained either by means of springs or a dead weight. The Pusey and Jones plastometer, which represents the dead-weight type, is quite unwieldy for rapid routine tests. On the other hand, the spring type of instrument is

easy to operate and speedy enough for production tests or for checking shipments. However, probably the most widely known instrument of this type is limited in accuracy, not only within a single instrument itself, but also when comparing one instrument with another. This is brought forcibly to our attention by frequent statements on purchasing specifications for automotive mechanical rubber parts, such as "the hardness of this part shall be such and such a value, as determined by or on the instrument in this laboratory." A subcommittee of Committee D-11 (on rubber products) of the American Society for Testing Materials is making a study of hardness-testing instruments of the penetration type and sponsoring the development of a dead-weight instrument for use primarily as a reference standard. It will probably be found desirable for the A. S. T. M. instrument to be sufficiently flexible for routine testing also.

Without further discussing the advantages and disadvantages of the various penetration types of instruments, it will suffice here to state that "hardness" figures in this report were obtained by means of the Firestone penetrometer (8). This instrument measures the amount of penetration of a ball point of standard size, subjected to a definite load obtained by means of an accurately calibrated spring. Penetration values are directly measured and accurately indicated in thousandths of an inch (A. S. T. M. hardness values per specification D314-29T).

Although the penetrometer is invaluable for certain work, hardness data are not satisfactory for judging the cure of a part. This is shown in Figure 2. The average penetration values of slabs marked in code were used in plotting this curve. It is seen that in passing from an undercure of 60 minutes to an overcure of 112 minutes at 148° C. the penetration varies only four points, which is well within the tolerance on most specifications. However, the penetrometer is valuable in checking cured slabs of this stock (No. 4), and also many other stocks, in that each cure will have a penetration value within certain narrow limits and any appreciable variation will indicate an error in the compound room or the mill room.

The writer has previously shown (1) that, although two motor parts of different size were cured from the same batch of stock to the same hardness (supposedly the same state of cure, as determined from theoretical considerations), they varied greatly in their ability to resist flexure under compression. This suggests that perhaps "hardness" as commonly determined by a penetrating instrument and "stiffness" or "rigidity" of a stock are not synonymous. However, the writer has always contended that the expression "hardness," particularly as applied to automotive rubber mechanical goods, *should* be used to designate the actual stiffness or deflectability as determined by a suitable compression test.

Large slabs often vary considerably in hardness (penetra-

tion). Theoretically, of course, all portions have received the same cure. Since penetration instruments produce low elongations, it has been considered that modulus data (and perhaps tensile) might likewise show up differently on such portions of the slab. To date it has been possible to show only a shade of difference, if any, in the modulus and tensile values for such portions. Data already obtained tend to show that the softer portions possess a slightly lower modulus at 400 per cent elongation. It is reasonable, of course, to assume that the variation in modulus at such elongations would probably be very small if the variations in hardness were due to but slight differences in cure of the surface tested.

Note—Since presentation of this paper, proof has been secured that there is no difference in cure as determined by combined sulfur data, but probably hardness variations are due to different stress conditions at the surface at various places in the slab owing to variations in stressing (flow) during cure.

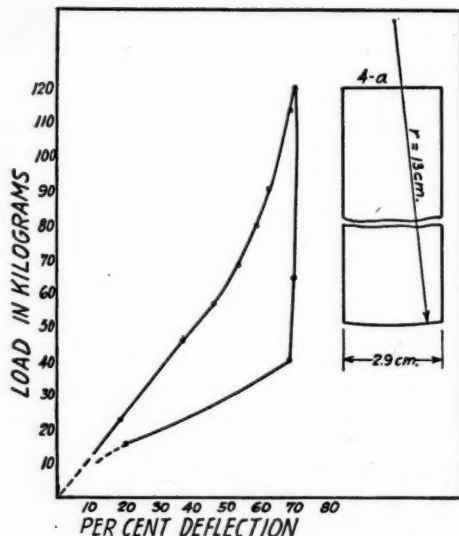


Figure 4—Large Hysteresis Effect of Small Plunger

Figure 3 shows load-deflection curves (I and II) of two disks of a stock of hardness values 73 and 64, respectively. Tests were made on round disks of 1.9 cm. (0.75 in.) diameter. It will be noted that the maximum deflections under 42 kg. per sq. cm. (600 lbs. per sq. in.) are practically identical, although from the penetration data one would hardly expect such results. The energy absorbed during loading is less for the test piece of high penetration. The hysteresis area is likewise somewhat lower.

Note—The area beneath the deflection curve and that between the deflection and the recovery curves are called, respectively, "relative energy of loading" and "relative hysteresis area" throughout this article, inasmuch as such data have not been converted into absolute units of energy.

Additional proof that hardness as determined by a penetrating instrument does not necessarily specify the true stiffness (hardness) of a stock is given in Table I. Tests 1 and 2 show decidedly different maximum deflections for both sizes of test disks, although there was no difference in penetration. On the other hand, 1 and 3, both on optimum cures as determined by maximum tensile, possessed the same stiffness, or maximum deflection data on both disks. Tests 2 and 4, an undercure and an optimum cure, respectively, differ widely in penetration but show no difference in maximum deflection at 182 kg. (400 lbs.) on a round disk of 6.45 sq. cm. (1 sq. in.) area. However, at 42 kg. per sq. cm. (600 lbs. per sq. in.) on a 1.9-cm. ($\frac{3}{4}$ -inch) disk there is a difference in the maximum deflection values.

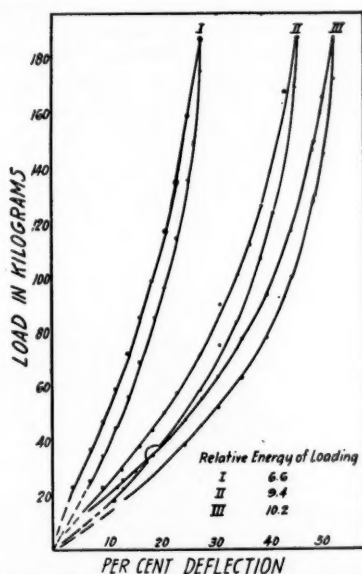


Figure 5—Effect of Gage on Compression Tests

Table I—"Hardness" vs. Deflection

TEST	STOCK	CURE AT 148° C.	PENE- TRATION	MAXIMUM DEFLECTION	
				At 42 kg./sq. cm. on 1.9-cm. disks	At 28 kg./sq. cm. on 2.9-cm. disks
		Minutes	0.001 in.	Per cent	Per cent
1	1	70	60	49.8	34.1
2	2	30	60	52.2	41.2
3	11	90	50	50.2	34.2
4	3	90	99	61.5	43.1

We can thus assume that two stocks entirely suited for a given purpose might possess the same deflectability in a given test, yet vary beyond certain specified penetration values. This can readily be seen from curves *a* and *b*, Figure 3. These

are theoretical curves for possible high- and low-modulus stocks that would possess approximately the same maximum deflection. Such curves which cross or meet after starting out with definitely different slopes are not unusual in compression tests. Indeed, Somerville and Ball (7) have shown that stress-strain curves based on tensile data likewise may cross.

Influence of Size of the Test Piece on Compression Tests

The size of the sample under compression influences both the accuracy of the individual tests, and accuracy depending on the "spread" between the results of different tests. The principal source of error in the first case is "cupping" or actual difference in size of the dies. The degree of cupping will depend upon the contour of the face of the die, method of applying the load, condition of the surface of the sample and die (whether wet or dry), and gage of the test piece. The possible errors in results due to an error of 0.076 cm. (0.031 in.) in the diameter of the test piece due to cupping or size of the die vary from 12.3 per cent on a disk of 1.9 cm. (0.75 in.) diameter to only 5.5 per cent on a 2.9-cm. (1.14-in.) disk.

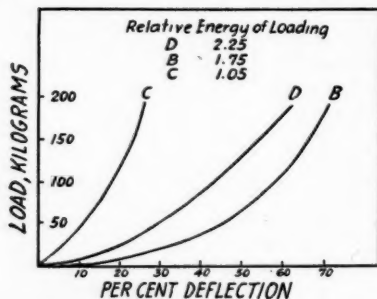


Figure 6

Cupping on a 1.9-cm. disk of a pure-gum stock (No. 1 of the present A. C. S. Physical Testing Committee) has been found to amount to 0.127 cm. (0.05 in.) on a sample of 0.72-cm. (0.285-in.) gage. Evidently the standard test piece should be more than 1.9 cm. (0.75 in.) in diameter. It will be readily seen, however, that the larger the test piece the less will be the spread between results. A careful consideration of the various factors involved is necessary before setting a standard.

The use of plungers (anvils), rather than subjecting the whole test disk to the compressive load, eliminates the error due to the cupping effect but may involve even more serious errors. Cutting due to sharp edges of the plungers is quite serious at relatively high loads, and this influences slippage. In addition, different test pieces are subjected to different stresses per unit volume by use of the plunger. Consequently, at high distortions at least—i. e., loads of 42.2 kg. per sq. cm.—on small plungers of 1.9 cm. (0.75 in.) diameter and even slightly larger, the test is so severe that it produces ab-

normal compression results. It is true that motor supports and other parts assembled under compression are commonly considered as loaded to a constant load per unit area—or, owing to the low percentage deflections to a constant load per unit area—but in reality they are assembled at practically constant deflection. A 5.9-cm. (2.32-in.) round disk cut from a slab of motor-support stock No. 5 of 0.545-cm. (0.214-in.) gage was deflected only 7 per cent by a load of 227 kg. (500 lbs.). Therefore, tests on disks large enough to insure sufficient accuracy are much more comparable to service conditions and fairer to all grades of stock than the constant-area tests as secured by plungers. Furthermore, the percentage distortion in tests at constant load per unit volume is more in line with service assembly compression.

In a further effort to show that it was advisable to use a test

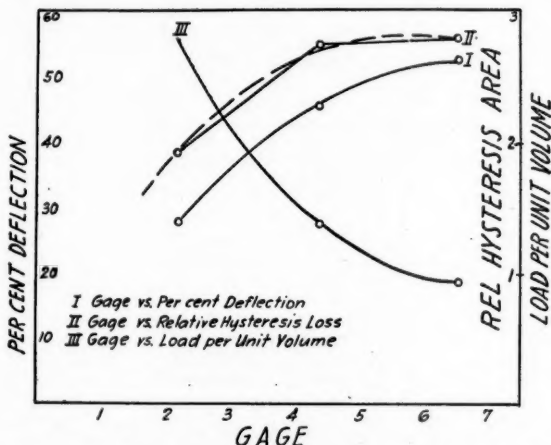


Figure 7—Effect of Gage on Per Cent Deflection Relative Hysteresis Area, and Load per Unit Volume

piece of larger diameter than the 1.9-cm. (0.75-in.) round disk a series of tests was arranged wherein the area under compression varied from 2.94 sq. cm. (0.44 sq. in.) to 11.4 sq. cm. (1.77 sq. in.). In order to eliminate the variable introduced by cutting the samples by means of a steel die, the steel plunger method was used. In each case a square test piece was cut of such a size that the area was 8.05 sq. cm. (1.25 sq. in.) greater than the contact area of the plunger, in order to get approximately the same supporting action by the surrounding rubber. It is possible that the amount of overhang should be based upon the relative circumferences of the test pieces under compression rather than be set at the same excess area. The results are reported in Table II.

The hysteresis data were secured by plotting percentage deflection against load. A more complete analysis would involve the use of both loads per unit area and loads per unit volume. In general, a small plunger shows a larger hysteresis

Table II—Effect of Various Sizes of Plungers on Square Test Pieces of Same Area of Overhang
(Stock No. 6, cured 12 minutes at 160° C.; all tests at 19.3 kg. per sq. cm. (275 lbs. per sq. in.))

DIAMETER OF PLUNGER	AREA UNDER LOAD	GAGE	VOLUME UNDER LOAD		FINAL GAGE LOAD	MAX. (FINAL) LOAD	LOAD PER CC. BASED ON:		INCREASE IN LOAD	MAX. DEFLEC- TION	RELATIVE HYSTERESIS LOSS
			Original	Final			Original thickness	Final thickness			
Cm.	Sq. cm.	Cm.	Cc.	Cc.	Cm.	Kg.	Kg.	Kg.	Per cent	Per cent	
1.9	2.84	0.595	1.69	1.27	0.447	550	32.4	43.0	32.7	24.8	0.6
2.38	4.45	0.564	2.51	1.89	0.425	863	34.2	45.5	33.0	24.8	2.45
2.90	6.45	0.595	3.84	2.87	0.435	125	32.4	43.5	33.6	25.2	5.4
3.81	11.40	0.587	6.7	5.55	0.485	222	32.7	39.7	21.1	17.3	4.55

value than actually exists. This increased hysteresis area with the smaller plungers may be explained somewhat on the basis of the increased load per unit volume and also by means of an experiment with a very thin sheet of pure gum. If such a sheet is stretched with the finger nearly to the point of rupture, it is found that the stresses are somewhat similar in effect to surface tension—viz., the small volume of rubber over the end of the finger tends to form to the rounded portion of the finger and seemingly to cling to it. At very high loads a plunger of 1.9 cm. (0.75 in.) diameter has penetrated the rubber to such a degree that the test piece seems to cling to the plunger as the loads are released, and consequently there is a high hysteresis area. The proof of this theory is found in experiments run on small plungers at much higher loads. In Figure 4 we see that the unloading curve descends abruptly for a considerable period, causing a large hysteresis area. When the major portion of the load has been released, there is an abrupt decrease in the distortion value. This point indicates the stress above which the sample clung to the plunger. The lower maximum distortion and the high hysteresis area for the largest plunger show that the slippage factor influences the results greatly.

This effect in the use of the plunger is decidedly detrimental, and plungers of small size, particularly at high loads, have been found to give greater errors than buttons or disks cut from flat sheets. Although the corners might be rounded to a certain extent for all anvils, the question of uniformity of this construction presents a serious objection. It would seem that a more satisfactory type of plunger would be a round disk with a convex contact surface. As a suggestion, there could be used a plunger 2.9 cm. (1.14 in.) in diameter with a suggested radius of curvature for the convex surface of approximately 15 to 25 cm. (6 to 10 in.) based on the center line of the plunger (Figure 4-a). Slippage variables could be largely eliminated by using vaseline to lubricate the plunger.

These facts show that considerable care must be used in judging a stock by its hysteresis data unless full details of the test method are known.

Effect of Different Shapes of Plungers

Undoubtedly the rubber surrounding the plunger during test exerts a supporting action on the volume of rubber directly underneath the plunger. In order to find out if this supporting action varied with different shapes of plungers the following tests were performed. In each case a test piece 3.2 cm. (1.5 in.) square was used. The various plungers were placed on the center of the respective test pieces. In the case of the square plunger, the sides were parallel to those of the test piece. The data are given in Table III. Although the maximum deflection data at 28 kg. per sq. cm. (400 lbs. per sq. in.) for the round disk, the square block, and the annular ring increased, in the order named, nevertheless these

values check within 3 per cent distortion. The 2.9-cm. (1.14-in.) round disk of rubber suffered the same maximum deflection as the sample with the annular ring, although in the latter case the maximum load was 43 per cent greater. Evidently the test volume under the ring was able to carry this 43 per cent increase in load because of the supporting action of the rubber not directly under the plunger.

The slightly greater maximum deflection found in the test with the annular ring over that for the other plungers can be explained on the basis of flow into the hole in this plunger.

Factors Influencing Slippage and Consequent Effects on Deflection and Hysteresis Data

Birkitt and Drakeley (3) have shown that the percentage deflection is dependent upon the ease of slipping at the surfaces of the test piece and the testing equipment, and also that, with almost perfect slippage as secured by vaseline, variations in the thickness have little or no effect on the maximum percentage deflection. Although it is true that there is at most very low slippage in the assembly compression of motor supports and many other parts, slippage certainly does condition the results of deflection tests. It is later shown that considerably more slippage occurs with a chromium-plated surface than with the polished steel surfaces. To date all routine tests of deflection comparisons in the compressometer have been conducted with the test piece in contact with polished steel surfaces. These are cleaned before each test with a metal polish, the surplus of which is immediately wiped off with a clean dry cloth.

Undoubtedly test pieces arrive in the laboratory with the surfaces in a different condition. Some of them may be oily or greasy, either naturally or as a result of contact with such materials. In order to learn the effect of such surfaces and also the effect of cleaning them, tests were conducted with a disk that had been sponged off with benzene and also on a similar disk from the same slab which was not sponged off. (Table IV)

Table IV—Effect of Sponging Off Surface of Test Piece with Benzene (Stock No. 2 cured 30 minutes at 148° C.)

GAGE	SURFACE	DEFLECTION AT:			RELATIVE HYSTERESIS AREA	LOAD TO DEFLECT 18.7 %
		5.55 kg. per sq. cm.	28 kg. per sq. cm.	42 kg. per sq. cm.		
Cm. In.		%	%	%		Kg. Lbs.
0.61 0.240	Sponged ^a	21.2	51.2	57.5	1.6	13.6 30
0.612 0.241	Natural	25.3	51.0	56.9	0.3	10.5 23

^a An undercure (highly bloomed) was used, but the test piece was not sponged sufficiently to remove all the bloom.

The greatest difference is noted at low loads per unit area, while at very high loads the results are very close. Probably the outstanding effect was that the hysteresis area of the unsponged sample was much less than that for the sponged

sample. This is entirely in keeping with the theory of the effect of slippage—poor recovery due to friction.

Unless otherwise specified, all the tests recorded elsewhere in this paper were on test pieces with the natural surfaces.

Effect of Thickness on Compression Tests

The influence of gage on compression testing has been ignored in the literature, with the exception of the work of Birkitt and Drakeley (3). Although their paper pointed out that the percentage deflection under equivalent loads per unit area is the same for test pieces of different gage provided perfect slippage occurs, it seems doubtful if gage variation has been generally considered as a source of error in specifications requiring such tests. The data in this paper are offered because in compression testing of motor supports or similar products little slippage actually occurs and, as previously mentioned, practically no slippage occurs in the service assembly.

Table V gives some data on two stocks that have been cured in a press in large slabs approximately 1 meter square. The slabs were cured 20 minutes at 160° C. (320° F.). It will be noted from the penetration data that the test disks showed no difference in cure (a poor criterion), although in the case of stock No. 7 it is quite possible that the thicker portion was enough below the cure of the thin section to give the results noted. However, the nature of stock No. 5 was such that the optimum cure (maximum tensile) could have been obtained anywhere from 14 to 20 minutes at the temperature used. Consequently, it is doubtful if the thicker portion of this stock is undercured or the thinner portion overcured. It will be noted that the thicker portions gave deflection values consistently higher than those for the thinner test pieces. This is to be expected when we consider that we have not provided for slippage of the test pieces over the contact surfaces of the testing equipment. Consequently a thicker sample will have more freedom of movement than a thinner sample (on a percentage-volume basis). The same general result is found in the study of compressive loads on short versus long columns.

Another peculiarity is that the hysteresis area of the thin test piece was always greater than that for the thick piece. There are two possible explanations for this. In the first place, the thinner test piece was subjected to a greater load per unit volume—i. e., greater fatiguing stresses. Elementary mechanics furnishes the second explanation. It is known that a body which least resists a force is the least affected permanently by that force. Therefore, the thin pieces must have offered greater resistance to the deflecting force, for we find that they were deflected a lesser amount. In other words, there was a greater ratio of stress to strain in the thinner than in the thicker test piece. Because of this, it is to be supposed that the thinner samples were under a somewhat greater

fatiguing action. In addition, it is known, that the thinner section actually was subjected to greater stress per unit volume than the thicker one, yet, as noted previously, was deflected to a less extent (was in a condition of less strain) principally because of less slippage per unit volume. Furthermore, in this case the ratio of deflection due to slippage and actual deflection of the rubber inside the test piece is greater for the thin test piece. Hence, there is less tendency to recover upon unloading, with a consequent greater hysteresis area.

Table V—Effect of Gage on Compression and Hysteresis Data

STOCK	CURE AT 160° C.	PENE- TRA- TION	GAGE		DEFLECTION AT:		RELATIVE HYSTERESIS AREA
					5.55 kg./ sq. cm.	28 kg./ sq. cm.	
		<i>Min. 0.001 in.</i>	<i>Cm.</i>	<i>In.</i>	<i>Per cent</i>	<i>Per cent</i>	
					1.9-cm. round disk		
	20	88-9	0.627	0.247	25.5	47.4	1.0
		90	0.765	0.301	27.9	50.9	0.5
5	20	...	0.606	0.239	15.1	36.0	3.5
			0.740	0.291	16.8	41.9	2.85
					2.9-cm. round disk		
7		88-9	0.660	0.260	18.0	38.5	4.0
		90	0.772	0.304	18.7	40.5	1.5
5		...	0.615	0.242	8.26	30.1	7.1
			0.726	0.286	7.7	31.8	6.8

Further proof of the above theory as to why a thick test piece suffers less hysteresis loss than a thin sample is found in the action of a pure-gum stock as compared with a highly compounded stock. In general, the pure-gum stock has a lower hysteresis loss, at least for the first hysteresis loop and even in the flexometer test, because it resists the compressing force to a lesser degree and also offers less internal resistance to molecular re-allocation. In Table VI are recorded some data for the load-deflection curves of a pure-gum stock (No. 2) and the same stock loaded with 15 volumes of carbon black (No. 9). In each case the 30-minute cure was an undercure. The loading curves for the disks 1 and 3 were almost identical (absorption of the same amount of energy) with the same maximum deflection. Nevertheless the relative hysteresis area of the pure-gum stock was 0.3 as compared with 2.75 for stock No. 9. In each case the 60-minute cure was approximately the optimum, yet for the pure gum we note a decided increase in the hysteresis area, whereas there is very little increase for stock No. 9.

At first it would seem that no further proof of the above explanation is necessary. However, in the following series the opposite relation is shown for the hysteresis data. An explanation is presented with the data.

In the above series of tests the question of identical cure arises, particularly when the gage variation is considerable. In order to avoid this difficulty, it was decided to take 2.38-cm. ($1\frac{5}{16}$ -in.) disks of 0.55-cm. (0.94-in.) gage slabs of stock No. 8 cured 25 minutes at 160° C. Deflection and hysteresis

data were first obtained on a single disk, then on a sample piled two disks high, and finally on a third sample three disks high. The piled samples appeared under load as single thick disks. However, it is known that greater slippage must have occurred between the rubber surface in contact with rubber than between the rubber-to-metal surfaces. Proof of this is given later from compression-set tests conducted under similar conditions. The data of these tests are given in Table VII with curves in Figure 5.

Table VI—Load-Deflection Data for Pure-Gum Stock (No. 2) and Stock Containing Carbon Black (No. 9)
(1.9-cm. round disks at 120 kg.)

STOCK	DISK	CURE AT 140° C.	PENETRA- TION	GAGE		MAX. RELATIVE DE- HYS-TERE- FLEC- SIS TION AREA	
				<i>Min.</i>	<i>0.001 in.</i>	<i>Cm.</i>	<i>In.</i>
2	1	30 (under)	105	0.557	0.241	56.9	0.3
	2	60 (opt.)	100	0.562	0.243	61.8	3.9
9	3	30	84	0.593	0.257	56.8	2.75
	4	60 (opt.)	74	0.565	0.244	52.0	3.05

From this table we can see that increased gage means greater percentage deflection and greater hysteresis area, in spite of the fact that the thicker disks carried smaller loads per unit volume. This last may seem quite anomalous until consideration is given to some possible curves as shown in Figure 6. If two stocks give deflection curves as in *D* and *B* (a hard and a soft stock, respectively) yet are both fairly deflectable, it is seen that it is entirely possible for the stiffer stock, *D*, to possess a higher hysteresis loss than the more deflectable stock; especially if it is assumed that complete hysteresis loss occurs at the maximum deflection. On the other hand, in case of a very stiff stock which deflects only a small amount and suffers 100 per cent hysteresis loss after reaching maximum deflection, as in curve *C*, it is easily possible for the hysteresis loss to be less than that for a highly deflectable stock, *D* or *B*. It is assumed that these tests are all conducted to the same maximum load. The application to the tests in Table VII is very easy merely by assuming that these curves apply to disks of different gage instead of disks from different stocks. The major cause of the higher hysteresis loss for higher gages is, however, the increased resistance to slippage (as in Part II).

The data in Figure 7 show that per cent deflection, relative hysteresis area, and load per unit volume in constant maximum-load tests vary with gage (data shown in Table VI and Figure 5). Curve I shows that the percentage deflection, as well as the hysteresis area, is approaching a maximum with increase in gage.

The outstanding feature of the whole matter is that the hysteresis area depends on the cure, the gage, the slippage, and

Table VII—Effect of Gage on Compression Tests

GAGE	TOTAL VOLUME UNDER COMPRESSION	MAX. DEFLECTION AT 32 KO.	RELATIVE HYSTERESIS AREA	RELATIVE ENERGY OF LOADING	LOAD PER UNIT VOL.	No. of LAYERS
<i>C_m.</i>	<i>I_n.</i>	<i>C_c.</i>	<i>C_u in.</i>	<i>Perc cent</i>	<i>K_s/cc.</i>	<i>Lbs./cu. in.</i>
0.55	0.216	2.46	0.15	27.8	7680	2780
1.1	0.436	5.92	0.30	45.8	3810	1380
1.65	0.651	7.38	0.45	52.7	2580	933
						1
						2
						3

Table VII—Effects of Repeated Deflection
[Original gage 0.63 cm. (0.249 in.); final gage, 0.625 cm. (0.246 in.)]

Loop	DEFLECTION AT:				LOAD LOSS AT MAX.	LOAD TO DEFLECT (1.5 CM.) 24%	RELATIVE HYSTERESIS AREA	LOAD DROP AT:					
	22.6 kg.	163 kg. (max.)		0.05 cm.				0.10 cm.	0.15 cm.				
		C_m	I_m							C_m	I_m	C_m	I_m
1	0.025	0.010	0.165	0.065	150	390	17.7	17.7	27.2	60	33.6	74	
2	0.025	0.014	0.163	0.065	135	283	17.7	17.7	27.2	60	33.6	74	
3	0.033	0.014	0.165	0.065	297	303	8.4	9.1	12.0	25	17.2	36	
9	0.033	0.013	0.165	0.065	138	303	8.1	7.7	14.1	31	15.0	33	

the location of the load-deflection curve. It is again evident that great care is needed in judging a stock by hysteresis data.

Effect of Extreme Cold in Deflection and Hysteresis Tests

Additional proof of the preceding discussion is found in tests run on a sample at normal temperature and then subjected to severe cold. The sample, which was tested cold, naturally had stiffened up considerably and consequently suffered less deflection; in other words, it resisted the compression force to a greater extent. It was found that the hysteresis loop for low temperatures was greater than for higher temperatures. In the tests here recorded a sample of No. 10 stock was cut from a shock insulator. This test piece was cut for flexometer tests (1) and was 1.43 cm. (0.56 in.) wide by 4.12 cm. (1.63 in.) long by 2.86 cm. (1.13 in.) high. The lower end of the compressetometer together with the test piece was immersed in a mixture of carbon dioxide snow and acetone for several hours previous to the test. Changes

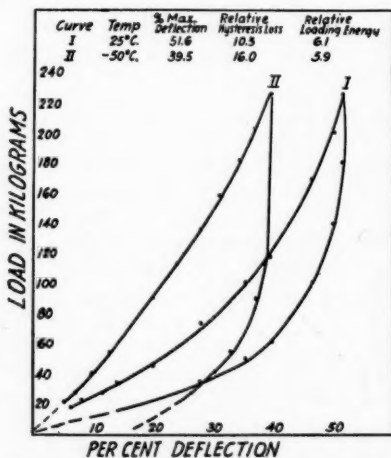


Figure 8—Low-Temperature Compression Test

in the freezing mixture were made from time to time to keep the temperature at approximately -50°C . The curves for the deflection tests on this sample, both at normal and at low temperature, are shown in Figure 8.

At extremely low temperatures, as is to be expected, the deflection curve, from the beginning, is much more nearly a straight-line function of the compressing load than the curve for the higher temperature tests. The loading curve shows a similarity to that of a steel spring. In other words, the rubber very nearly obeys Hooke's law. This is the only example of this phenomenon encountered in the work herein

reported, and is only relative, for the size of the test piece and conditions of the test determine the relation between the load and the deflection for any given stock. However, owing to the great hysteresis loss of this sample (for a single impact or compression) it has greater absorbing power than the spring because the spring would recover directly. The tests on the cold sample were made after it had been tested at room temperature.

In Figure 8, although there was considerable difference in the percentage deflection at the maximum load, the energy of loading, as measured by the comparative areas under the loading curve for each case, was approximately the same. The relative return of energy as measured by the area of the loops was approximately 60 per cent less for the cold sample.

In order to determine whether the rubber suffered any serious effects from this test, the test piece was taken immediately from the cooling solution and run in the flexometer at 50 per cent distortion. The test piece rapidly warmed up to approximately 70° C. and after 10 minutes' flexing was removed. No failure or appreciable set could be detected.

In the above it was assumed that the previous test at room temperature on this sample had no effect on the piece as later tested in the cold. These tests were run 24 hours apart. This assumption is justified as shown by data presented in the next section. Furthermore, data on impact tests on bumpers, given in Part II of this paper, show that very little change in hysteresis loss occurred after several hundred deflections at 54 per cent distortion.

Effect of Repeated Compression on Results of Compression Tests

Repeated hysteresis tests under compression show a similarity to repeated stretch tests (6) in that the greatest area is found for the first loop and reaches a fairly constant value for the third loop. Undoubtedly, continual fatigue occurs to a greater or less extent depending on the stock. A direct comparison of data of repeated tensile tests with data of repeated compression tests cannot be made without considering the question of the relative loads per unit volume and whether repeat tests have been made at constant maximum load or constant maximum distortion.

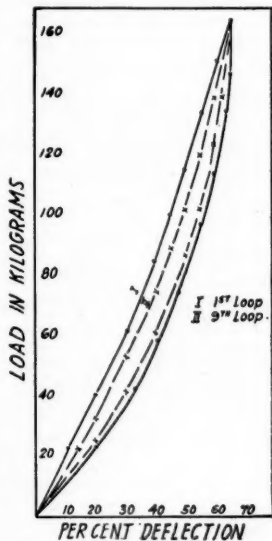


Figure 9—Repeated Compression Tests

Table VIII gives deflection and hysteresis data for the first, second, third, and ninth tests on 2.3-cm. round disks of stock No. 4 cured to the optimum. The original area of this test piece was 4.16 sq. cm. (0.645 sq. in.) and loadings were to 38.5 kg. per sq. cm. (550 lbs. per sq. in.). The hysteresis loss or area in the first loop is shown to be considerably greater than that for the second loop, which in turn is somewhat greater than that for the third loop. In other words, the hysteresis loop is continually getting smaller, but very little difference is noted after the third cycle has been made. The data for load loss, which is the drop in load at maximum loading for 1 minute, show that this stock is fairly resistant to fatigue effects. The values for load drop represent the respective decreases in load, for the given distortions, for the unloading curves as compared to the loading curves, and are an indication of the relative decreases in hysteresis areas with repeated deflection. Figure 9 shows the curves for the first and for the ninth hysteresis loop. It will be noted that the ninth loop falls entirely within the first. These data are typical of those obtained in many similar tests.

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Part II—Compression-Set and Some Special Tests

In Part II the main factors necessary to be considered in formulating a compression-set test are described and a proposed compression-set test is briefly outlined. The constant-load test is preferable to a constant-deflection test. To secure the true relative properties of stocks, it is recommended that the surfaces be lubricated with vaseline. Tests for special cases, such as the flexometer test and an impact test for bumpers, are also described.

AS MENTIONED in Part I, many automobile mechanical rubber parts are assembled wholly or in part under compression. In the first class are motor supports, body and fender shims, radiator pads, spring shackles, torque insulators, etc. Axle and spring bumpers, grommets, tubing, and other parts are so installed that portions of them are under compression to a greater or less degree,

and so belong to the second class. All such parts in time acquire permanent set as a result of compressive forces. Set under compression has been considered of such serious consequence that motor-car manufacturers insist that such parts shall withstand some sort of a compression or permanent-set test. Unfortunately there are a great many such tests requested in specifications, although they all aim to determine the same answer—namely, the quality of the part tested. Under properly controlled conditions a single test can be made to furnish all the information desired which is the resistance of the part to permanent set when under a compressive load.

Constant Distortion vs. Constant Load

Compression-set tests can be made under conditions of constant distortion or constant load. Although the former is the simpler, particularly as regards equipment, the writer believes that permanent-set tests on the various stocks or rubber parts to be assembled under compression should be conducted under constant load.

Probably one of the simplest devices for the test at constant distortion is made from two parallel steel plates clamped together by means of four bolts passing through the plates near the corners (*A*, Figure 1). The distortion of the test piece is determined by holding a scale beside the clamp. This is a grievous source of error. In *B* (Figure 1) a step toward greater accuracy has been made in providing a constant zero point for measuring the distance between the two plates. The scale can be put flush on the bottom plate and thus there is a single point of error in measuring the distortion. Even these distortion measurements are probably not accurate to within ± 0.025 cm. (0.016 in.). This is only a 6 per cent error based on a gage of 0.635 cm. (0.250 in.) for the test piece. But the slope of the load-deflection curves for a 1.9-cm. (0.75-in.) round disk near the maximum load in a standard test conducted at 42 kg. per sq. cm. (600 lbs. per sq. in.) is much greater than the slope at the low loads. The above maximum load produced a deflection of 0.322 cm. (0.127 in.) on a test piece of stock No. 6 cured 12 minutes at 160° C. (320° F.). An error in the maximum distortion of but ± 0.025 cm. (0.01 in.) would amount to a variation in the load from 107 kg. (236 lbs.) to 136 kg. (300 lbs.). These data correspond to deflections of 0.298 cm. (0.117 in.) and 0.348 cm. (0.137 in.) taken from load-deflection curves. This is a variation in load of approximately 12 per cent. An additional variable—drop in load due to fatigue—also exists.

Consider the case of a soft and a harder stock, each compounded and used for motor-support service, and also of a third stock which is much stiffer yet likewise a high-quality stock. Some relative compression data for these stocks are given in Table I.

If all tests were conducted at 37.3 per cent deflection, a load of 120 kg. (265 lbs.) would be imposed on stock No. 11, whereas less than two-thirds of this amount would be imposed on stock No. 5. Stock No. 14 is even more deflectable and at 18.7 per cent deflection it carries only approximately one-fourth the load carried by No. 11. Inasmuch as the gage of the No. 11 sample was about 16 per cent greater than that for the other samples, this stock was favored in the series and a sample of approximately 0.57 cm. (0.225 in.) gage would have required a higher load than 120 kg. (265 lbs.) for 37.3 per cent deflection as used in the above comparison.

In tests run at a constant maximum load the actual loads per square centimeter under a maximum load of 120 kg. (265 lbs.) show that No. 11 is being stressed only 38 per cent more than No. 14, instead of 350 per cent more as was the case in tests under constant distortion.

In order to consider the constant-load tests to have been made at the same load per cubic centimeter, let us assume that the original gage of all stocks was the same. This would mean that those stocks which in the table have a gage higher than No. 14 would actually show in the table even greater variations from that stock. To summarize, a soft stock experiences a less load per unit area due to a greater percentage deflection, but the same load per unit volume. This decrease in load is nearly proportional to the final area resulting from a decrease in thickness. On the other hand, in the case of constant-deflection tests the hard stock may require three to four times as much load, or even more, to deflect to the same amount as the soft stock. If, as above, we assume that all stocks in Table I had the same original gage, the figures in the last two columns will represent loads per unit area during test.

Compression-Set Clamp

The above discussion has disregarded actual changes or fatigue of the test piece during the test. For both constant load by spring clamps and constant distortion the stock which suffers the more rapid fatigue will be benefited to the extent that it will be resisting the smaller final load per unit area. This effect is negligible in a properly designed spring clamp, as has been shown by tests in the compressetometer. Evidently a constant-load device is a necessity. If a spring clamp is used, a suitable means for measuring deflection of the springs (loads) is likewise a necessity.

Probably the simplest type of constant-load equipment is based on one of the constant-deflection clamps described above. If the tie bolts are longer, a short compression spring can be inserted between the plates of the clamp. The test piece is then put on a steel disk placed on top of the spring and loaded by compression of the spring. Here again there is a fairly large error in measuring by means of an ordinary

Table I—Comparative Deflection of Hard and Soft Stocks^a Loaded to Maximum of 42 Kg. per Sq. Cm. (600 lbs. per Sq. In.) Based on Original Area

Stock	Cure	HARDNESS (PENETRATION) Kg.	MAX. DEFLECTION AT 120 Kg.	GAGE		VOLUME	FINAL AREA	ACTUAL LOAD PER SQ. CM. AT MAX. LOAD OF 120 Kg.	RELATIVE LOAD TO GIVE DEFLECTION OF:	
				Orig.	Final				18.7% ^b	37.3%
	Min.	° C.	0.001 in.							
14	25	320	100	0.562	0.254	1.6	6.3	19.1	8.2	37.8
5	12	320	63	0.576	0.315	1.64	5.2	23.0	18.2	68.2
11	60	298	38	0.68	0.426	1.93	4.55	26.5	36.4	120.0

^a 1.9-cm. (0.75-in.) disks used.

^b Approximate assembly deflection of a certain car support, but on larger areas.

loose scale or caliper and scale. One such type of set clamp which has come into use has a short clutch spring about 7 cm. (2.75 in.) long, which distorts 0.95 cm. (0.38 in.) under 120 kg. (265 lbs.) load. It has been shown that percentage deflection increases during tests by an amount equivalent to the fatigue of the test piece. This may amount to as much as 0.127 cm. (0.05 in.) on a 0.635-cm. (0.25-in.) sample, and may cause an error of approximately 13.0 per cent based on the spring distortion of 0.95 cm. (0.38 in.).

In order to provide an easier operating and more accurate device, the writer designed the small compression-set clamp shown in Figure 2 (also shown in Figure 1, Part I). This clamp is provided with a spring 10.1 cm. (4 in.) long, which deflects 1.9 cm. (0.75 in.) at 120 kg. (265 lbs.). The error due to the change in distortion caused by the fatigue of the sample has been cut 50 per cent. Likewise the percentage

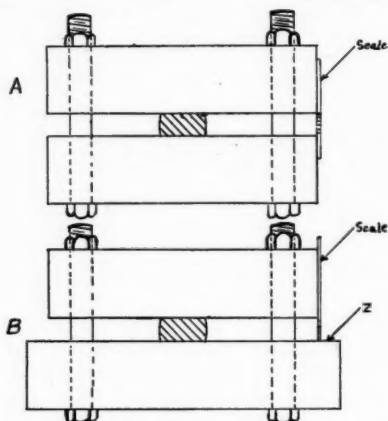


Figure 1—Constant-Deflection Compression-Set Clamps

A—Double zero-error
B—Constant zero-setting at Z

error arising from an error in measuring this spring deflection has been decreased. For convenience the clamp is provided with a depth gage with a scale graduated in hundredths of an inch. The gage is rigidly attached to the clamp, and hence is much more satisfactory than a loose scale. Load-deflection data are then obtained for each spring and suitable curves are constructed so that the clamp can be set to a definite scale reading for a given desired load. A magnifying glass is used in reading the scale. A single nut control increases the ease of operation and permits uniform deflection throughout the test piece.

Comparison of Tests Using Plunger and Rubber Disk

It can readily be seen that both the constant-deflection clamp and the constant-load clamp can be used to test either small buttons cut direct from the samples (constant-volume

tests) or to make constant-area tests by means of a small plunger or anvil. The relative merits of the plunger versus the round rubber disk method were discussed in Part I. The same arguments against the plunger are valid here. Some comparative compression-set tests were also made.

All tests were started in clamps originally at room temperature and were of 66 hours' duration at 70° C. All test pieces were 1.9 cm. in diameter and were cut from the same slab of stock No. 14, cured for 50 minutes at 148° C. The load was 42 kg. per sq. cm. (600 lbs. per sq. in.). All disks were sponged off with benzol and dried. The original gage was determined by a R. & S. gage with 1-cm. (0.39-in.) diameter foot, the final gage by a B. & S. No. 2 micrometer caliper 0.396-cm. (0.16-in.) diameter foot after a 30-minute recovery. In the exceptional case of a warped disk the average of the minimum and maximum gage was measured 0.15 cm. (0.08 in.) from the edge of the disk.

The results are given in Table II. The final load per unit volume is 59.4 per cent greater in case of the plunger method with an increase of 40 per cent in permanent set. This would tend to show that percentage increase in set is not in the same ratio as percentage increase in load per unit volume and hence the error is slight for small differences in the latter. In addition, "cupping" occurs in the lower side of the test piece in the plunger method at high loads (over 42 kg. per sq. cm. or 600 lbs. per sq. in.). This should preclude the use of an ordinary thickness gage unless it is provided with a small foot and also a small pedestal to support the test piece.

Dead-Weight vs. Spring Compression-Set Clamps

Without doubt a properly arranged dead-weight equipment should be more nearly capable of 100 per cent accuracy in load than the spring clamp. However, in order to eliminate frictional "wobble" troubles such equipment should be vertical acting, as in Figure 3, *A*, instead of "horizontal acting" as shown in *B*. A dead-load device is unwieldy and liable to error due to a sudden application of the load (slip-

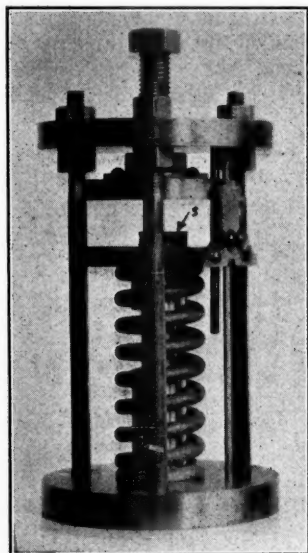


Figure 2—Compression-Set Clamp
S—Test disk

page errors). For testing a piece 12.9 sq. cm. (2 sq. in.) in area at 28 kg. per sq. cm. (400 lbs. per sq. in.) using 364 kg. (800 lbs.), for example, some hydraulic or pneumatic equipment would be much more convenient than the actual weight method. However, for the sake of simplicity and for practical accuracy, the constant-load spring clamp is very satisfactory when properly designed, and the adoption of some fairly compact device, such as shown in Figure 2, would be an important step forward in the program of unification of methods of testing.

Table II—Comparison-Set Tests Using Disk and Plunger

CLAMP	MINIMUM GAGE			SET	VOLUME		LOAD PER CC.	
	Orig.	Final	Loss		Orig.	Final	Orig.	Final
	<i>Cm.</i>	<i>Cm.</i>	<i>Cm.</i>	<i>%</i>	<i>Cc.</i>	<i>Cc.</i>	<i>Kg.</i>	<i>Kg.</i>
DISK:								
1	0.658	0.470	0.178	28.6	1.87	1.87	1050	1050
2	0.674	0.508	0.166	24.6	1.91	1.91	1040	1040
				Av. 26.6				
PLUNGER:								
1	0.665	0.420	0.245	37.0	1.85	1.19	1045	1670
2	0.665	0.417	0.248	37.4	1.85	1.118	1045	1670
				Av. 37.2				

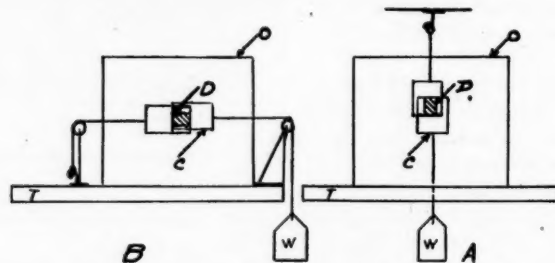


Figure 3—Dead-Weight Constant-Load Clamps

O—Oven
T—Table

D—Test disk
C—Telescopic test clamp

The question has been raised as to the effect of repeated use on the calibration curve of the springs used in the constant-load clamps. Figure 4 shows that deflections of a new spring at 120 and 182 kg. (265 and 400 lbs.), respectively, were 1.7 and 2.59 cm. (0.67 and 1.03 in.), whereas after almost 3 months of continual use at loads between these two values for periods varying from 22 to 72 hours at 70° C., the distortions were, respectively, 1.9 and 2.76 cm. (0.7 and 1.09 in.). Of course other calibration curves were necessary in the meantime, but most of the change occurred within the first few tests at the higher load, and hence probably could have been avoided by a dead-weight test before calibration. It is considered that most of this change occurred in the thin ground-down portions of the last coil at each end of the spring.

Another question has been raised as to the variation between calibration at room temperature and at the standard

test temperature (70° C.). In Figure 5 it is shown that at 182 kg. (400 lbs.) there is less than 0.038 cm. (0.015 in.) weakening at 70° C. as compared with the value at 24° C., whereas at 120 kg. (265 lbs.) there is practically no error. This is quite within the experimental error in most spring clamps in use.

It has been claimed (private communication to the author) that the spring clamp gives higher compression-set results than the dead-load method "due to the stiffening action resulting from the heat-expansion of the spring." Others have maintained that heat tends to weaken the spring. The latter view is strengthened by the curve in Figure 5.

In fact, the variation due to temperature in the load-deflection curve of the type of spring used in the clamps shown is probably far within the other errors inherent in any small, compact non-precision instrument of this type.

Note—For present purposes a precision instrument is considered only as one which will measure distortions of load or gage of the sample to within 1 per cent and 0.0025 cm. (0.001 in.), respectively.

It is true that there is an apparent stiffening of the spring during a compression-set test which may amount to as much as 0.127 cm. (0.05 in.) increase in

length at 120 kg. (265 lbs.) in tests on 1.9-cm. (0.75-in.) disks cut from slabs of approximately 0.635-cm. (0.25-in.) gage. This is due, however, to fatigue of the stock, and in fact the load is really falling instead of increasing. Some data are given in Table III. The tests were conducted at 70° C. at 136 kg. (300 lbs.) on 2.9-cm. disks of 0.95-cm. stock. The error in load is less than 3 per cent, and is less on lower gages and at higher loads. For two samples tested simultaneously the error is doubled.

It was shown in Part I that the load falls when test pieces stand under constant distortion due to the fatigue in the rubber. Even greater fatigue occurs in the constant-load spring clamp, because the load is greater than that necessary for a constant-distortion test. A large change in distortion

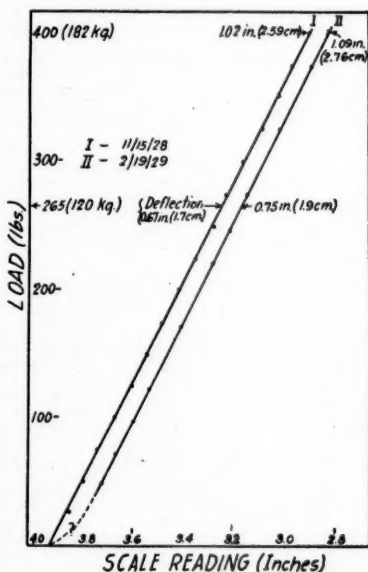


Figure 4—Calibration of Constant-Load Spring

of the test piece allows the spring to expand slightly with an appearance of stiffening; hence the load in a spring clamp is continually decreasing with increasing fatigue, but this load drop is quite negligible. Since the load drop is doubled if two samples are tested in the same clamp, only one test should be made at one time in each clamp.

The accuracy of spring calibrations as determined by data obtained from tests on 1.9-cm. pieces tested at 42 kg. per sq. cm. for 24 hours at 70° C. in different clamps is shown in Table IV. All the disks were cut from the same slab of stock (No. 15 cured 20 minutes at 160° C.) and readings were checked independently by two observers. Final gage measurements were made by a small-foot (No. 2) B. & S. micrometer caliper.

Table III—Error in Spring Load Due to Failure of Test Piece

CLAMP	SAMPLE GAGE	SET	COMPRESSED LENGTH OF SPRING			HEIGHT OF SPRING AT 136 KG.	AV. INCREASE IN LENGTH
			Orig.	Final	Increase		
	<i>Cm.</i>	%	<i>Cm.</i>	<i>Cm.</i>	<i>Cm.</i>	<i>Cm.</i>	%
1	0.965	11.1	7.62	7.7	0.08	2.135	3.0
2	0.966	9.2	7.6	7.65	0.05	2.135	

Table IV—Comparison of Accuracy of Calibration of Various Clamps

CLAMP	GAGE			SET
	Original	Final	Loss	
	<i>Cm.</i>	<i>Cm.</i>	<i>Cm.</i>	%
A-1	0.702	0.572	0.030	18.5
	0.695	0.562	0.033	19.1
A-2	0.691	0.550	0.041	20.6
	0.695	0.565	0.030	19.0
B-1	0.675	0.542	0.033	19.9
B-2	0.678	0.542	0.036	20.2
B-3	0.678	0.526	0.052	22.5
B-4	0.695	0.555	0.040	20.4

These data indicate that the calibration curves for the various springs used were very accurate. The duplicate tests in clamps A-1 and A-2 likewise show very satisfactory agreement when tests are made at different times in the same clamps.

The slope of the spring-calibration curve has a definite effect on the accuracy possible with the constant-load clamp. It is doubtful if any spring should be used at test loads of 182 kg. (400 lbs.) or under if the slope of its calibration curve is greater than that noted in this paper. Owing to the increased relative distortion at low loads due to the ground-down spring ends, the slope is arbitrarily set for data between 120 and 182 kg. (265 and 400 lbs.). Thus the original slope of the calibration curve (Figure 4) for the spring was 3.86, whereas the final value was 3.97. A maximum value of 4.5 might be set, but is probably high, and any value lower than 3.75 prevents use over a wide load range.

For high-load clamps this laboratory is using springs calibrated to 455 kg. (1000 lbs.) with a maximum slope of 6.5.

Note—Since presentation of this paper clamps of 1800 kg. (4000 lbs.) capacity have been secured.

Influence of Gage and Slippage and Factors Influencing Slippage

Variation in the gage of the test piece has an enormous effect on permanent-set tests under compression. The effect on single disks of variable gage is magnified in tests conducted on pieces formed by "piling" disks. Table V gives data of permanent-set tests conducted similar to deflection tests recorded in Table VII, Part I, except that the set tests were of 24 hours' duration at 70° C. under 188 kg. (414 lbs.) in the compressetometer.

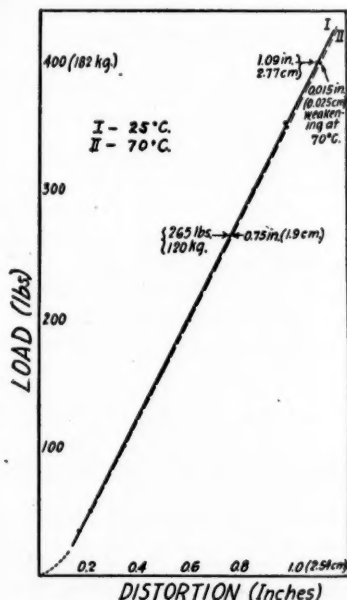


Figure 5—Effect of Heat on Spring Calibration

Greater slippage (distortion) occurred at the rubber-to-rubber surfaces and evidently the increase in area of the middle disk on test 3 alone accounts for the increased set, for it was subjected to less load per unit area and also per unit volume than specimens in tests 1 and 2. In Part I it was shown by percentage-deflection data that lubricated samples distorted the most, as a result of surface slippage. Evidently control of slippage is of prime importance in true set tests as well as true deflection tests.

Various surfaces affect the slippage to different degrees. Accordingly compression-set tests were made to determine

the effect of a lustrous chromium plate on polished steel. In one experiment two test disks of 1.9 cm. diameter were separated by a bright chromium-plated spacer during tests in polished steel clamps. In each case the final diameter of the surface in contact with the steel plate was 1.9 cm., whereas that in contact with the chromium surface was 2.16 cm. This represents over 22 per cent increased area with the chromium surface. Practically no slippage occurred at the polished steel surface.

Table V—Influence of Gage Variation on Compression-Set

TEST	ORIGINAL GAGE		VOLUME UNDER LOAD	RELATIVE LOAD PER CC.	COMPRESSION-SET	
	Each disk	Total			Each disk	Total average
	<i>Cm.</i>	<i>Cm.</i>	<i>Cc.</i>	<i>Kg.</i>	<i>%</i>	<i>%</i>
1	0.508	0.508	2.30	80	19.6	19.6
2	0.488	0.958	4.26	62	23.2	24.6
	0.470				26.0	
3	0.445	1.251	5.57	32.6	30.0	34.4
	0.361				43.2	
	0.445				30.0	

Table VI shows set data obtained when both surfaces of the test pieces were in contact with polished steel and bright chromium-plated surfaces, respectively. In this laboratory bright chromium-plated contact surfaces have been made a standard because it is easier to keep them in a uniform condition. All constant-load clamps have been chromium-plated all over. The results are so satisfactory that such a procedure is recommended for adoption as standard.

Table VI—Relative Influence of Steel vs. Chromium-Plated Surfaces in Set Tests

A. S. T. M. hardness stock No. 1. Load, 120 kg.
Test specification, 20 hrs. at 70° C. Diameter of disk, 1.9 cm.

CLAMP	GAGE			SET	SURFACE
	Orig.	Final	Loss		
	<i>Cm.</i>	<i>Cm.</i>	<i>Cm.</i>	<i>%</i>	
A-1	0.726	0.596	0.13	17.8	Chromium plate
A-2	0.726	0.615	0.11	15.4	Steel

Birkitt and Drakeley (3, Part I) reported more nearly ideal slippage in deflection tests when pieces were lubricated with vaseline but they made no mention of set tests. Table VII shows the increased set resulting from the use of a thin film of white vaseline on the round 1.9-cm. test disks subjected to 42 kg. per sq. cm. for 24 hours at 70° C. as compared with normal tests.

Here again set is affected more by the physical distortion, or relative displacement within the test piece, than by load per unit volume or unit original area. Consequently, in a test to determine the true deflectability and set the rubber should be lubricated.

Duration of Compression-Set Tests

Increased duration of the test naturally produces increased set, but there seems to be nothing gained by setting up a standard of duration greater than 22 hours at 70° C., which is universally accepted as the standard aging temperature. Table VIII shows the values for percentage set on 1.9-cm. disks of stock No. 16 (cured 25 minutes at 160° C.) when subjected to 120 kg. for various periods at 70° C.

Table VII—Effect of Lubrication of Test Piece

CURE AT 148° C.	COMPRESSION-SET	
	Normal surface	Vaseline
<i>Minutes</i>	%	%
30	17.3	27
45	16.6	26.5
60	14.7	18.7
75	15.8	20.4

Table VIII—Effect of Duration of Tests on Compression-Set

TEST	DURATION	ORIGINAL GAGE		COMPRESSION-SET (AV. OF 2 TESTS)
	<i>Hours</i>	<i>Cm.</i>	<i>In.</i>	<i>Per cent</i>
1	8	0.62	0.245	14.3
2	21	0.615	0.242	24.25
3	25 ¹ / ₂	0.617	0.243	25.5
4	48	0.62	0.245	31.0
5	72	0.62	0.245	37.0

Inasmuch as daily routine tests are often desirable, this laboratory is standardizing on a 22-hour test. This allows a 2-hour change-over period, which is sufficient to take care of several clamps and allows the clamps to reach room temperature, which is desirable for the sake of uniformity. The 22-hour standard will facilitate testing by speeding up tests and in having a definite time each day for the work.

Measurement of Original and Final Gage of Test Pieces

The measurement of the final gage after subjecting the test piece to the compressive load is very important. In most methods cupping occurs on the top or bottom surface or both, as a result of slippage. In all tests in this laboratory, and those herein reported except tests with the ring method mentioned later, the original gage has been measured by a Randall and Stickney gage with a 1.9-cm. (0.75-in.) diameter foot acting under a dead load of 200 grams (0.44 lb.), whereas the final gage was obtained by a No. 2 Brown and Sharpe micrometer 30 minutes after removal from the test apparatus. Samples were allowed to cool on an oak desk top.

This recovery period has been considered ample for ordinary test procedure. No trouble is experienced in getting checks with the B. & S. micrometer caliper even by different operators. In order to compensate for the lack of a pressure-

foot load, 0.001 inch (0.025 mm.) is deducted from the reading obtained by the touch system. If the distortion has been uniform, as required in this laboratory and made possible by the single-nut control constant-load clamps, little experience is necessary for the operator to get the minimum gage reading that just allows no-load slippage between the micrometer feet. A small-foot R. & S. gage with a similar small-foot pedestal or table for the test piece is necessary for accurate work if the micrometer is not used, but the latter is more economical and just as accurate if made a standard procedure. The No. 2 B. & S. micrometer is not satisfactory for measuring the gage at the center of test pieces of large diameter because the anvil does not protrude far enough from the frame. A micrometer similar to B. & S. No. 30 R. & S. is needed, but with a micrometer larger than the No. 2 the accuracy has been impaired.

Other Permanent-Set Methods

Where service assembly involves compression a compression-set test is more logical than any type of tension-set test, whether at repeated constant distortion or repeated constant load. The procedure of holding at either a definite elongation or elongating load and then determining the set after a certain recovery period likewise finds small favor for, although such tensile methods may differentiate between stocks, only by checking against set results under compression or actual service is it possible to find out if such results have any meaning as to service under compression. After all, shims, supports, and similar parts fail principally due to one or two causes (or both)—namely, structural deterioration or loss in gage.

A cold-flow test depending upon exudation of rubber through the opening in an annular ring has occasionally been used in place of the compression-set test. The ring test finds little to warrant its adoption because:

(1) The flow into the opening depends upon the condition of the edges of the ring surfaces and of the rubber and ring.

(2) The flow occurs early in the test and, although it is more or less permanently held owing to the conditions of the test, it is not necessarily a criterion as to whether or not the support will suffer compression-set, inasmuch as in service assemblies usually very little percentage flow occurs.

(3) There are inaccuracies inherent in the method of measuring the relative displacement into the hole in the ring.

(4) The necessary sample—at least greater than the 3.44 cm. (1.355 in.) o. d. of the ring—cannot be secured from many automotive rubber parts.

(5) The test requires 48 hours to give a percentage value for the cold flow equivalent to that secured in 24 hours by the disk method. Lessening the time would greatly decrease the accuracy of the ring test and is inadvisable.

Requirements of a Compression-Set Test

A satisfactory compression-set test should be formulated only after due consideration of the following factors:

MATERIAL TESTED

- (1) Within what limits of thickness do samples fall?
- (2) Within what limits of hardness do samples for a particular product fall?
- (3) Is any consideration taken of such ingredients as paraffin, etc., which might give a surface with a lubricating effect?

TEST PIECE

- (1) What is the size (diameter or other dimensions) of the test piece?
- (2) How are the test-piece dimensions secured? Are they (a) molded; (b) cut by a steel die, by blow with a hammer, or by pressure as in an arbor press; (c) cut by a cork-borer; or (d) by the spinning or motor-drill method?
- (3) Is the slab or die wet before the test pieces are cut?

TESTING CLAMPS

- (1) Does the device produce constant distortion?
- (2) Does the device give a constant load obtained by springs? Are the springs inside or outside of the oven, and what is the load-deflection ratio of the spring?
- (3) Does the device give a constant load obtained by dead weight, and is the test piece assembled in a horizontal or vertical position?
- (4) What is the speed of (a) compression; (b) releasing the load?
- (5) Is slippage in the clamps controlled by (a) lubrication of contact surface; (b) a polished contact surface; or (c) plated (chromium, etc.) contact surfaces?
- (6) Is the clamp at room temperature or test temperature when the test pieces are inserted and the load is applied?
- (7) If a constant-distortion device, how is the distortion measured?
- (8) If a constant-load device, how is the load measured?
- (9) What kind of an oven is used in the test? Is the temperature automatically controlled, and is the air changed regularly or circulated by a fan?

OTHER CONDITIONS OF TEST

- (1) What are the temperature limits of the test?
- (2) How long is the test (22 to 72 hours, etc.)?
- (3) Is the test piece removed from the clamps at once after removal from the oven?
- (4) Does the test piece recover on glass, wood, or a metal surface?
- (5) How soon after removal from the clamp is the final gage measured?
- (6) How is the final gage measured (R. & S. gage or micrometer caliper)? State the size of both contact feet or surfaces of the gage.
- (7) Can the method be universally adopted without highly complicated equipment?
- (8) Are there any special factors peculiar to the part to be tested or to the laboratory equipment that must be considered?

Suggested Method for Compression-Set Test

Cut two round disks of the same gage, preferably less than 1.27 cm. (0.5 in.) from the part in question by means of a steel die with an arbor press, giving accurately an area of 1 sq. in. (6.45 sq. cm.) without lubrication of the test piece or die. Compress between bright chromium-plated surfaces in a constant-load clamp at room temperature to 28 kg. per sq. cm. (400 lbs. per sq. in.). The maximum slope of the load-deflection curve of the spring for providing the

load shall be 4.5 for a 182-kg. (400-lb.) spring or 6.5 for a 455-kg. (1000-lb.) spring.

Keep the clamps with the test piece in a 70° C. oven provided with a fan for air circulation for 22 hours, and then immediately remove the test piece from the clamp. Take the final gage at the center of those test pieces which are not

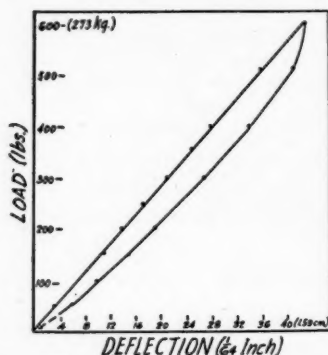


Figure 6—Shear Hysteresis

irregularly deflected by means of a small-foot micrometer caliper similar to B. & S. No. 2 not less than 30 or more than 35 minutes after removal from the testing device. Compression-set is reported as the percentage decrease in gage based on the original thickness as determined by the standard Randall & Stickney gage or No. 2 B. & S. micrometer caliper.

For true comparative results of the quality of the stocks test disks should be lubricated, but this involves difficulties not worth encountering except for research and stock development since service compression is without slippage. Hence lubrication of the test disk is not included in the above.

Additional Tests on Auto Mechanicals

In the automobile assembly most rubber parts used under compression, particularly those used to absorb vibration, suffer, in addition to the compressive load, repeated dynamic stresses of impact, flexure, or shear, or perhaps all three. Flexure, impact, and shear tests have been used in this laboratory for evaluating such parts as spring shackles and torque insulators, bumpers, and certain types of motor supports. Figure 6 shows the load deflection, or shear, curve obtained in a test on a vertical type of metal-rubber motor support which is fast replacing compression supports.

Figure 7 shows a device for repeated compression tests on bumpers. Various stocks, cured in the form shown in A, are subjected to 44 impacts each minute, either for a definite period or until failure occurs. In the former case hysteresis and deflection tests, before and after the test, are used to judge the ability of the stock to withstand impact. Most tests have been run at approximately 54 per cent deflection, which for stock No. 11, cured 60 minutes at 147° C., required 590 kg. (1300 lbs.). Some data obtained on various cures of three stocks are given in Table IX. In every case the maximum deflection at the 227-kg. (500-lb.) load increased as a result of the impact test, whereas there was a decrease in the relative hysteresis area. Com-

paring the optimum cures of the first two stocks, it will be noted that stock No. 11 showed less change in hysteresis loss than stock No. 12. The former is the more efficient stock. Furthermore, the relative drop in hysteresis loss with increased cure was less for No. 11 than for No. 12. Even though the optimum cure of No. 11 was impacted for 5 hours, the relative hysteresis loss was intermediate between the lower and higher cures. In the case of No. 12 the 5-hour impact test had increased the change in hysteresis loss beyond that obtained for either the under- or the overcure, indicating that this stock had absorbed more internal energy, or at least had acquired a certain amount of set, and consequently was requiring less energy per deflection as the test progressed. The 45-minute cure of No. 12 had started to fail before the end of the 5-hour test. This is taken as further proof of the logic of the hysteresis theory especially when we consider that no failure occurred with the 40-minute cure

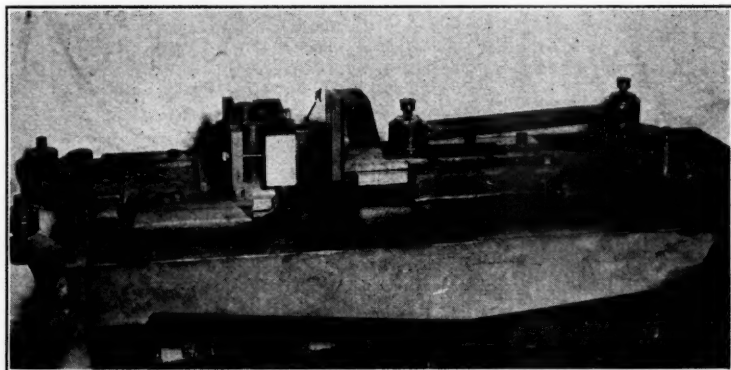


Figure 7

of No. 11 when impacted 7 hours more. Likewise the drop in hysteresis loss in this latter case was no more than for the overcure.

In the case of stock No. 13 failure had occurred before the end of the $1\frac{1}{2}$ -hour impact period. This test piece is shown in Figure 7.

It might prove more sound technically to impact the bumpers under constant load or to a constant energy absorption value each time. However, the matter of imposing actual loads of approximately 455 kg. (1000 lbs.) at the rate used in this test offers serious difficulties for the ordinary laboratory type of equipment. Furthermore, if a compounded stock meets other requirements for motor-support stocks, it should be satisfactory for bumpers if it passes the above impact test.

In the case of No. 11 and No. 12 the results should be entirely comparable, particularly for the optimum cures,

Table IX—Repeated Compression Tests on Bumper Stocks—44 Impacts per Minute

STOCK	CURE	PENETRATION		DURATION OF IMPACT AT 54%	MAXIMUM DEFLECTION AT 227 KG.		APPROX. RELATIVE HYSTERESIS LOSS		DECREASE IN HYSTERESIS AREA
		Before impact	After impact		Before impact	After impact	Before impact	After impact	
	Min.	0.001 in.	0.001 in.	Hours	%	%	%	%	%
11	40	54	49	1 1/2	32.4	33.9 ^a	43	36	7 ^a
	60	50 ^b	50	5	29.6	32.5	50	41	9
	80	53	50	1 1/2	32.8	33.8	54	43	11
12	30	49	48	1 1/2	28.6	31.4	47	38	9
	45	48 ^a	47	5 ^c	28.4	30.3	52	38	14
	60	49	50	1 1/2	30.2	32.8	56	45	11
13	20	55 ^a	55	1 1/2	38.5

^a The maximum deflection and relative hysteresis loss values after 7 hours' additional impact were 33.4 and 32 per cent, respectively.^b Considered as optimum cure.^c Had "failed" (internal crack up from bottom and also in from the side) before the end of a 5 hour test.

for they showed the same stiffness as determined by load-deflection data.

For shock and torque insulators and also the vertical type of motor supports, the flexometer test, with or without compression to correspond to service conditions, is undoubtedly valuable, and laboratory tests have been made on this basis. Results of the flexometer tests have been found much more satisfactory than tests on the entire shackle.

The above-mentioned impact and flexure tests require special equipment and consequently are not recommended for the general run of automobile mechanicals assembled under compression, but rather only for special products. For motor supports, body shims, and similar parts it would seem advisable, as previously stated, to perform tests such as deflection and compression-set, since these can be performed on the parts themselves or on test pieces cut therefrom.

Notes

(1) Tests recorded in this paper have been on stocks of moderate or relatively good resistance to compression-set. For torque-resisting purposes under compression, stocks have been developed with practically no set as determined by the method suggested.

(2) Trouble has not been taken to make metric units (obtained as slide rule derivations of standard English data) check perfectly, since the slight discrepancies do not interfere with the point to be proved.

(3) Committee D-11 of the A. S. T. M. has approved a tentative method of test for the hardness of rubber. This is published in the 1929 Proceedings of the society (D314-29T).

Acknowledgment

The writer wishes to acknowledge his indebtedness to E. B. Babcock, Erle C. Zimmerman, and N. A. Shepard, who have coöperated to make possible the investigations herein reported.

Recovering Lead in Rubber Factory

F. L. Haushalter

B. F. GOODRICH CO.

When we say that lead melts at 621° F. and has a tensile strength of 1900 lb. per sq. in., we have in mind pure lead that has not been remelted many times in crucibles that are not always clean. This metal, too, as ordinarily used in pipes and conduits has been drawn; stresses have been set up in the lead by this process, and their magnitude depends upon several factors, such as temperature of extrusion, extent of oxidation, rate of cooling, and impurities accumulated in the remelting.

Where lead is melted and extruded onto wire and hose the tensile strength of such lead, when removed from the wire or hose, has increased to about 2400 lb. per sq. in. The percentage elongation, however, has decreased from about 50 to about 25. Industries where lead is used again and again by remelting, as in the rubber industry, where hose is vulcanized in a lead casing, the casing removed after vulcanization of the hose and remelted, the problem of controlling the physical properties of the lead becomes a serious one.

After pure lead has been extruded onto the hose and the tensile strength thereby stepped up to about 2400 lb. per sq. in., the tensile strength then falls appreciably below the original value of 1900 lb. per sq. in. as soon as the vulcanization process begins, with the temperature of vulcanization at 280° F. When the samples of lead as s'ripped from the hose after vulcanization were tested for tensile strength at various temperatures, the curve approximated a straight line. A stress-strain curve on the lead at a temperature of 280° F. indicates that at a tensile stress of about 600 lb. per sq. in. the lead begins to yield, for the curve departs from the original slope.

The curve for dross lead, or removed scum, shows a straight line almost to the breaking point, which occurs at less than 700 lb. per sq. in. The curve for refined dross—lead from which the scum has been removed by the ordinary process of ladling—shows good characteristics up to 900 lb. per sq. in., and then fails at little more than 1000 lb. per sq. in. Pure lead, from the pig, follows the straight line up to about 700 lb. per sq. in., then gradually departs from it, as one would expect. Samples removed from lead-covered hose before and after vulcanization indicated that the stresses have been somewhat relieved by the heat treatment, for the curve drops below that for pure pig lead, though the ultimate tensile strength is greater than that of the pure pig lead.

The following table indicates that the tensile values are practically the same:

	Tensile Strength, Lb. per Sq. In. at	
	80° F.	280° F.
Pure lead, pig	1880	1239
Lead tube, before cure	1930	1345
Lead tube, after cure	2390	1385
Refined dross, ready for production	1810	1118
Dross	400	650

By setting up a daily control test on the tensile strength of the lead a safe working stress of 600 lb. per sq. in. in the lead can be assumed. By using an internal pressure of 125 lb. per sq. in. on the hose and an external pressure of 35 lb. per sq. in. in the heater, the effective maximum pressure the lead must counteract is 65 lb. per sq. in. Using the formula $PD = 2tf$, where P = effective pressure (lb. per sq. in.), D = inside diam. of lead tubing, t = wall thickness (inches), f = 600 lb. per sq. in. working stress, a table of wall thicknesses for various hose diameters may be tabulated.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

**POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. I.
SOME EXPERIMENTS WITH ISOPRENE AND
BUTYRALDEHYDE**

BY J. B. CONANT AND C. O. TONGBERG

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In a preliminary paper¹ on the irreversible transformations of organic compounds under high pressure, some experiments were reported on the polymerization of isoprene and other unsaturated compounds at room temperature by the application of pressures of the order of magnitude of 9000 atmospheres. This work has been continued with the aim of discovering the factors which control the rate of polymerization under high pressures and the nature of the products formed. A great majority of the experiments were performed with isoprene since this substance polymerizes more rapidly than any other substance of this general type which is readily available; furthermore, the early observations showed that very erratic results were obtained with different samples of isoprene and we desired, if possible, to discover the catalytic substances which seemed to be responsible for the peculiar behavior. A few experiments also were performed with some other compounds and they will be discussed at the end of this communication. The pressure apparatus employed was kindly lent us by Professor Bridgman. We wish to express our appreciation of his kind coöperation, and the courtesy extended to us by the Director of the Jefferson Physical Laboratory of Harvard University in which the physical part of the experiments was actually performed. Manipulation of the

¹ P. W. Bridgman and J. B. Conant, *Proc. Nat. Acad. Sci.*, **15**, 680 (1929).

presses was performed by Mr. Zisman and without this valuable assistance the work would not have been possible.

The isoprene used in all of the experiments was prepared by the thermal decomposition of limonene by means of a hot wire, essentially according to the method described by Harries.² It was purified by distilling through an efficient column and had a boiling point of 36–38°. The material to be compressed was placed in small glass tubes and pressure transmitted by means of mercury in the apparatus referred to in the previous paper.¹ In most of the experiments the temperature of the press varied between 23 and 25°. The pressure was read by means of the usual device used by Professor Bridgman. The pressures recorded in this paper are usually given in even thousands and are significant within ± 100 –200 atmospheres. Unfortunately it was not always possible to hold the pressure at exactly the desired point; the actual variations of a few hundred atmospheres probably did not introduce serious errors in the work.

The extent of the polymerization in the case of isoprene was determined by removing the sample from the glass container (if necessary by breaking the container), rapidly weighing, and allowing the material to stand in air until constant weight was obtained. The amount of non-volatile material under these conditions was taken as a measure of the polymerization. This is, of course, only an approximate method but it sufficed for the purposes at hand. The greatest amount of polymerization which we ever observed was 92%. We obtained many figures running between 88 and 90. The fact that 100% was never recorded probably indicates a certain constant error in our method of procedure, although it may correspond to the difficulty of polymerizing the last traces of the isoprene.

It was clear at the outset of our work that the previous history of the isoprene was of great importance in determining the rate of polymerization; for example, some freshly prepared and distilled material was only 30% polymerized in twenty hours at 12,000 atmospheres, whereas some material similarly prepared and distilled which had then been allowed to stand for nine days at 2° in a bottle from which most of the air had been displaced by a stream of nitrogen, was 88% polymerized in the same time and at the same pressure. Oxygen catalysis was, of course, suspected, and the importance of this factor was shown by the fact that it was possible to increase the rate of polymerization by shaking the isoprene with oxygen and then allowing it to stand for some hours. The addition of peroxides, and particularly of pinene which had been shaken with oxygen, was very effective in accelerating the rate of polymerization. Hydroquinone, a well-known negative catalyst for reactions subject to oxygen

² C. D. Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," J. Springer, p. 142.

catalysis, had a marked effect on decreasing the rate; in fact, at 9000 atmospheres pressure it was possible to reduce the rate from 40% in twenty hours to less than 3% in the same time by the addition of about 0.1% hydroquinone. In this experiment a sample of isoprene was used which had been allowed to stand for some time in the presence of oxygen.

Although peroxide catalysis was found to play a very important part in the acceleration of the polymerization, it was not essential to the process. This was demonstrated by the fact that a sample of isoprene carefully distilled in an atmosphere of oxygen-free nitrogen and introduced into the apparatus without the admission of oxygen, nevertheless polymerized under a pressure of 12,000 atmospheres to the extent of 37% in forty-eight hours. It is interesting that at 12,000 atmospheres the presence of 0.1% hydroquinone only changed the rate by about 50%.

Our attempts to measure the effect of pressure and temperature on the rate of polymerization were severely handicapped by the difficulty of preparing uniform samples of isoprene. The use of freshly distilled material did not solve the difficulty as evidently varying amounts of peroxides were formed in an irregular fashion. This is illustrated in Table I. Our most consistent results were obtained with samples of isoprene which had been allowed to stand at 2° in nitrogen or air at least seven days and which then only slowly altered their intrinsic tendency to polymerize. For example, a sample from a given lot which had stood for one day after distilling was 34% polymerized in twenty hours; at the end of the third day another sample from the same lot was 64% polymerized in the same time; on the seventh day the rate had increased to 86% in twenty hours. Further standing up to eleven days seemed to be without effect. A sample from the same lot was freshly distilled on the ninth day and the rate of polymerization dropped from 88% in twenty hours to 25% in twenty hours. Another lot of material which was allowed to stand under practically the same conditions came to a fairly constant rate which was, however, different from the rate of the first lot; the new maximum rate was about 61% in twenty hours. Still a third lot gave final values nearer the first.

The most significant data which we have so far been able to obtain are given in Table II; the results were obtained with two different lots of isoprene which had stood for at least eight days. An inspection of Table II shows that duplicate experiments usually give very concordant results. This fact at first misled us into believing that it would be possible to determine the rate over the entire range with an accuracy of a few per cent. The results which we later obtained showed that the uncertainties due to catalytic effects, and also caused to a slight extent by the variations in pressure and temperature, made our probable error much greater than we had at first estimated. Some continuous method of following the

reaction with one sample for an extended period will have to be developed in order to obtain really satisfactory results.

TABLE I

POLYMERIZATION OF FRESHLY DISTILLED ISOPRENE

Each experiment recorded below was performed with a separate sample of material distilled within one hour of being subjected to pressure

Pressure, 12,000 atmospheres
Temp., 23-25°

Time of application of pressure, hours	Polym-erized, %	First order reaction constant, $k \times 10^3$
7	19	3.0
15.25	15	1.1
15.25	12	0.8
29	46	2.1
29	40	1.7
45	25	0.6
68	66	1.6

Av. 1.6

$$k = \frac{2.3}{t} \log \frac{1}{1-Z} \text{ where } t \text{ is in hours}$$

and Z is the fraction polymerized.

TABLE II

POLYMERIZATION OF ISOPRENE WHICH HAD STOOD IN NITROGEN CONTAINING A FEW PER CENT. OF OXYGEN AT LEAST NINE DAYS AFTER DISTILLATION

Pressure, 12,000 atmospheres
Temp., 23-25°

Time, hours	Polym-erized, % Lot 1	Reaction constant, $k \times 10^3$
5	27	6.3
5	33	8.0
5	35	8.6
16	83	11.2
20	87	10.2

Av. 8.9

Lot 2

5	11	2.3
20	61	4.7
23	66	4.7
23	65	4.6

Av. 4.1

In order to have some way of comparing the extent of the reaction at different times we have calculated a reaction velocity constant according to the usual first-order equation. The reaction is presumably one of high order but some autocatalytic effect makes the first-order constants actually increase somewhat with time instead of decreasing as would be expected. The result is that they may be used to characterize approximately the rate of the process, and we have used them for this purpose throughout this paper. Some experiments in which indifferent diluents were employed showed that the reaction was actually of an order higher than the first. For example, a sample of isoprene with which it normally took only ten hours for 65% polymerization, required twenty hours for the same extent of reaction when diluted with an equal volume of petroleum ether. The same material when diluted with 5.5 times its volume of petroleum ether or toluene was polymerized to the extent of 5 to 13% in fifteen hours; undiluted, only about one hour would have been required for the same degree of polymerization.

The catalyst which gave the most consistent results was a sample of pinene which had been shaken for four or five hours with oxygen and which was then used from time to time without further treatment. Definite amounts of this pinene were added to freshly distilled isoprene. The

results are summarized in Table III, the first order reaction constants being given as a rough measure of the rate of the polymerization. It is evident that the consistency of the results leaves much to be desired but in spite of their variation the effect of the catalyst is evident. The rates obtained with the smallest amount (0.001 per cc. of pinene, a concentration obtained by a dilution procedure) were probably not effective since the average rate of freshly distilled isoprene (Table I) was about the same. The larger amounts of catalyst had a very real effect, although this effect is not directly proportional to the amount; thus an increase of 20-fold in the amount of catalyst only doubled the rate. A few experiments with this same catalyst at pressures of 9000 and 6000 atmospheres indicated the same sort of effect although the results were very erratic at times.

TABLE III
CATALYTIC EFFECT OF OXIDIZED PINENE ON POLYMERIZATION OF FRESHLY DISTILLED ISOPRENE

Pressure, 12,000 atmospheres. Temp., 23-25°			
Amount of catalyst, cc. per cc.	Time, hrs.	Percentage polymerized	Reaction constant, $k \times 10^4$
0.1	4.5	83	39.3
.1	4.5	63	22.1
			Av. 30.7
.04	4.5	28	7.3
.04	4.5	41	11.7
.04	4.5	63	22.1
			Av. 13.7
.01	4.5	38	10.6
.01	4.5	12	2.8
.01	16.0	54	4.8
			Av. 6.1
.002	15.75	55	5.1
.002	15.75	55	5.1
			Av. 5.1
.001	4.5	7	1.6
.001	4.5	12	2.8
.001	15.0	24	1.8
			Av. 2.1

We carried out many experiments in an attempt to obtain sufficient information to enable us to give with some accuracy the pressure coefficient of the rate of polymerization; again we have employed the first order constants in comparing the rates. The results are summarized in Table IV. As in all the other work, we were confronted with the difficulty of obtain-

ing reproducible measurements. However, the average value of $k_{12,000}/k_{9000} = 3.5$ is probably of considerable significance. If we assume this value and calculate the ratio of rates for 6000 atm. and 2000 atm. compared to 12,000 from the relationship $\Delta \log k / \Delta P = \text{constant}$, the results are considerably lower than were actually found. Thus, for $k_{12,000}/k_{6000}$ we found 17 and 30 (Table IV, note) while the calculated value is 12. For 2000 atmospheres $k \times 10^2$ for uncatalyzed isoprene is 0.02 (about 2% in five days); this gives a value for $k_{12,000}/k_{2000}$ of about 100 against the calculated 67. As a rough first approximation the effect of pressure seems to be represented from 6000 to 12,000 by the expression $\log k_1 - \log k_2 = 1.8 \times 10^{-4} (P_1 - P_2)$. A very large increase of the pressure coefficient at lower pressures is indicated, however, by the few facts just given and by an extrapolation to atmospheric pressure. Using the equation just given the value of $k_{12,000}/k_1$ is 145 and taking $k \times 10^2$ at 12,000 as 10 (for isoprene after standing), $k \times 10^2$ at 1 atm. = 0.069. This value, which corresponds to 10% polymerization in ten days at 1 atmosphere and 23°, is certainly too large by at least a factor of 100 and probably by 1000 or more. The spontaneous polymerization of isoprene at room temperature and pressure appears to be so slow as to be capable of detection only after a period of years.³

TABLE IV

ESTIMATION OF THE PRESSURE COEFFICIENT OF THE RATE OF POLYMERIZATION OF ISOPRENE (TEMP., 23-25°)

Isoprene and catalyst (if any)	Average value of reaction constant		
	12,000 atm., $k \times 10^2$	9000 atm., $k \times 10^2$	$\frac{k_{12,000}}{k_{9000}}$
Freshly distilled	1.7	Less than 0.2	...
Lot 3, 9 days old	9.0	2.9	3.1
Lot 1, 14 days old	8.9	2.7	3.3
0.1 cc. of pinene	30	7.0	4.3
0.04 cc. of pinene	10	3.5	2.9
0.01 cc. of pinene	6	2.8	2.1
0.01 cc. of pinene	2	0.4	5.0

Av. 3.5

NOTE.—At 6000 atmospheres a value of $k \times 10^2$ for freshly distilled isoprene was found to be about 0.1 (3% in twenty-six hours), giving a ratio of $k_{12,000}/k_{6000} = 17$. With 0.1 cc. of pinene a value of $k \times 10^2 = 1.0$ at 6000 atm. was obtained (20% in twenty-six hours), giving a ratio of $k_{12,000}/k_{6000} = 30$.

³ Since this was written we have unexpectedly been in a position to obtain some additional information in regard to the pressure coefficient. Through the kind coöperation of Professor Bridgeman we have determined the rate of polymerization of isoprene at a pressure of approximately 18,000 \pm 500 atm. at 23°; the following amounts of polymer were obtained: 10% in twenty minutes; 76% in three hours; $k \times 10^2 = 52-65$. The same material gave the following values at other pressures: 6000 atm., $k \times 10^2 = 1.9$; 12,000 atm., $k \times 10^2 = 8.4$.

Since the publication of the preliminary paper we have discovered the claims of Herman Plauson to the polymerization of butadiene hydrocarbons at normal temperatures in a few days by applying pressures of the order of 500 to 600 atmospheres. An extrapolation of the results given above to those pressures is not at all consistent with Plauson's results.⁴ We have not attempted to repeat all of the six examples given in the Plauson patent but have tried the effect of 600 atmospheres' pressure at room temperature on a mixture of isoprene and dimethylbutadiene emulsified in gelatin solutions as specified and have been able to obtain only the merest trace of possible polymer after six days. Samples of dimethylbutadiene behaved similarly. We are thus unable to confirm the statement that the butadiene hydrocarbons may be polymerized at room temperature by the application of 600 atmospheres' pressure for five to six days.

The temperature coefficient of the rate of polymerization may be estimated from the data given in Table V. If these results are plotted in the usual way ($\log k$ against the reciprocal of the absolute temperature) the three points at 12,000 atmospheres fall on a straight line within the probable error. The value of the heat of activation (calculated from the usual equation) is of the order of magnitude of that of simple chemical reactions in solution at room temperatures. The difference in the values at the different pressures cannot be considered as definitely significant in view of the errors in our work. Such an effect may exist but many more experiments at the lower pressures will be necessary to prove it.

TABLE V
TEMPERATURE COEFFICIENT OF THE RATE OF POLYMERIZATION OF ISOPRENE UNDER PRESSURE

Isoprene employed	Average value of reaction velocity constant ($k \times 10^3$)			<i>E</i> calcd. from max. temp. range, calories
	(A) 12,000 atmospheres			
Lot 1 (stood for 13 days)	0.8 (0°)	9.0 (23°)	42 (41°)	16,300
	(B) 9000 atmospheres			
Freshly distilled +0.01 cc. of pinene	...	About 3 (23°)	37 (43°)	23,000
	(C) 2000 atmospheres			
Isoprene which had stood for 6 days	0.01 (23°)	1.5 ^a (62°)	6.3 (80°)	24,000

^a Freshly distilled isoprene +0.1 cc. of pinene; value perhaps considerably too high compared to those at 23 and 80°.

A comparison of the temperature and pressure coefficients shows that at the higher pressures and room temperature a change of 15° is about equivalent to 3000 atmospheres' pressure as regards the effect on the reaction rate. Over a wider range we estimate that raising the pressure from

⁴ U. S. patent 1,415,468 (May 9, 1922).

2000 atmospheres to 12,000 atmospheres increases the rate about 100-fold; this increase could also be obtained by raising the temperature from about 20 to 60°. If the temperature and pressure coefficients of the polymerization of isoprene are typical, it is clear that the mere acceleration of the reaction is more readily accomplished by raising the temperature than by increasing the pressure. However, there must be many cases (and the polymerization of isoprene is probably one) where the nature of the products differs according to whether they are formed at high pressures or elevated temperatures. This will evidently be the case when side reactions are possible which have a large temperature coefficient but negligible pressure coefficient. A future field of profitable inquiry into the *acceleration* of reactions by high pressures would seem to be with those complex reactions (such as polymerization) where certain side reactions might be avoided by operating at low temperatures and high pressures.

It has already been emphasized that the polymerization of isoprene under pressure is markedly subject to positive catalysis by oxygen and peroxides and to negative catalysis by hydroquinone. The effect of hydroquinone is more marked at 9000 atmospheres than at 12,000, though the effect of positive catalysts appears to be about the same at the two pressures. The most effective catalyst of all we found to be the isoprene ozonide. For example, if ozonized oxygen (about 5% ozone) was passed into isoprene for twenty minutes and the material then subjected to pressure, the substance was practically completely polymerized (88%) at 12,000 atmospheres in only five hours ($k \times 10^3 = 42$). Although ozone was very effective at this pressure we were disappointed in its action at lower pressures; for example, at 6000 atmospheres it was not so effective as 0.04 cc. of pinene, since in twenty-six hours' time slightly ozonized isoprene was only 5% polymerized. The action of oxygen itself on isoprene is rather peculiar. Freshly distilled material, if shaken with oxygen for a few hours and at once subjected to a pressure of 12,000 atmospheres, polymerizes at about the same rate as though the oxygen treatment had not been given (10–15% in five hours; $k \times 10^3$ about 1). On the other hand, if, after the oxygen treatment, the material is allowed to stand for one to two days, the rate of reaction is greatly accelerated (74–80% in fifteen hours; $k \times 10^3$ about 10). Samples of isoprene which had never been shaken with oxygen but which had stood either in air or nitrogen containing a little oxygen for many days could not be made to polymerize at a faster rate by shaking with oxygen before introducing into the press. From these facts it seems clear that the catalytic action of oxygen is primarily due to a peroxide which is slowly formed from the oxygen dissolved in the isoprene. If an organic peroxide is added directly as in the case of oxidized pinene, or if benzoyl peroxide is used, then there is no indication of an induction period being required. One may imagine that

the action of the peroxide is to cause the formation of a series of chain reactions according to the theory which has received such wide acceptance in recent years.

Nature of the Product

In all cases the product obtained at room temperatures was a transparent, colorless, rubbery solid. Its elastic properties, strength and particularly its solubility seemed to be a function primarily of the extent to which the polymerization had been allowed to proceed. Thus the material obtained in runs at 12,000 atm. where the reaction was 80% or more complete was slightly elastic and, though it showed no tendency to crumble, would not stand stretching more than twice its length without breaking. It was extremely insoluble; in fact, we have not found any solvent in which it would dissolve to any appreciable extent. A sample of it was continuously extracted with dry ether in an atmosphere of nitrogen according to the method given by Pummerer;⁵ after twelve hours only 1% had been extracted. On the other hand, material from an experiment in which the polymerization was only 30% complete behaved quite differently. After the evaporation of the unpolymerized isoprene the material was very elastic and tough. It could be elongated three to four times without breaking. It was more than 50% extracted by ether in twenty hours and in forty hours was at least 90% soluble. The slight residue was soluble in a benzene-piperidine mixture but not in pure benzene. The density of the polymerized material was about 0.9 as compared with 0.68 for isoprene; thus the volume change in the process is very considerable.

An experiment was performed in order to determine whether the volatile material in an experiment, in which the polymerization was incomplete, was wholly isoprene. The excess isoprene (about 50%) was removed by a stream of nitrogen which was then passed through a tube immersed in a carbon dioxide snow-ether mixture. The condensate was examined and found to be practically pure isoprene with only a trace of high-boiling material which had a terpene-like odor. This result, together with all the facts mentioned above, would seem to indicate that the polymerization of the intermediate products must proceed faster than the first step in the process which involves isoprene itself. The extreme insolubility of the completely polymerized material suggests that under these high pressures the reaction proceeds very far even at room temperature. We attempted to see if natural rubber itself would be rendered more insoluble by being subjected to pressure. We employed both crude sheet rubber and the material obtained by extracting this material with ether. In the case of the ether extract there seemed to be some change after subjecting to 12,000 atmospheres for many hours; the resulting material was somewhat less soluble,

⁵ Pummerer, *Ber.*, 61, 1583 (1928).

but the results cannot be regarded as conclusive. More work along this line is in progress. A solution of gutta-percha in toluene subjected to 12,000 atmospheres for some hours was apparently unchanged.

Experiments with Other Materials

The rate of polymerization of vinyl acetate is considerably less than that of isoprene; thus in twenty hours at 12,000 atm. the material was only a few per cent. polymerized and even after forty-eight hours only about 50% was converted to the polymer. The effect of oxygen on the rate of polymerization is much less evident than in the case of isoprene; indeed, it is not certain that this polymerization is subject to a positive catalytic effect of this sort. The oxidized pinene catalyst which we found so effective with isoprene had the reverse effect on vinyl acetate, decreasing the rate very markedly. Another strange effect is that the addition of a small quantity of hydroquinone instead of decreasing the rate increased it nearly 10-fold. Because of the long time required in order to obtain appreciable polymerization, the behavior of vinyl acetate was not studied in as much detail as isoprene since the time at our disposal was relatively short.

The peculiar behavior of *n*-butyraldehyde and isobutyraldehyde was referred to in the preliminary paper.¹ We have now studied the polymerization of *n*-butyraldehyde in a little more detail. The rate of polymerization is markedly increased by passing ozone through the material for about twenty minutes. Material thus treated was polymerized in twenty-five hours at 12,000 atmospheres to a hard solid amorphous mass without strength or elasticity. This material was evidently of high molecular weight as it was very difficultly soluble in alcohol, ether or other organic solvents. A softer material having the consistency of cheese was obtained by the action of 12,000 atmospheres for twenty-five hours on redistilled aldehyde. In this case the polymerization did not seem to have proceeded so far, since the material was soluble in alcohol. When the alcohol solution was poured into water the material was reprecipitated as an amorphous solid. Both the soft and the hard solids changed rather rapidly on standing at 25°, the eventual product being *n*-butyraldehyde. The change is definitely catalyzed by the presence of acids and somewhat retarded by the presence of pyridine. However, it was found impossible to keep the material at room temperature for more than about a day even when pyridine was added to it. This rapid reconversion hindered us greatly in studying the material. Attempts to obtain derivatives of the more soluble form by reactions with such reagents as *p*-nitrophenylhydrazine yielded only derivatives of *n*-butyraldehyde. It seems probable that the products obtained from *n*-butyraldehyde are polymers similar to the well-known polymers of formaldehyde (trioxymethylene). In the case of formaldehyde the energy relations are such that these polymers of high molecular weight

are stable substances at room temperature and pressure, whereas with the higher homologs the complex polymer is perhaps only stable at high pressures. The effect of pressure on the aliphatic aldehydes is in many ways the most interesting result of our work, since it is the one case which has discovered where a reaction can be brought about only by the application of high pressures. We seem to be concerned here not only with increasing the rate of a process but with an actual change of the equilibrium conditions.

Summary

1. The rate of polymerization of isoprene under high pressures has been studied. The reaction is subject to positive catalysis by peroxides and negative catalysis by hydroquinone. Although the reaction is of a high order, the rate is approximately in accord with a first order reaction presumably because of an autocatalytic effect. The temperature and pressure coefficients of the rate have been estimated. The solubility and elasticity of the product depend on the extent to which the isoprene has been polymerized; when the polymerization is practically complete at room temperature at 12,000 atm. the product is very insoluble

2. The action of high pressures on *n*-butyraldehyde produces a solid only slightly soluble in organic solvents. It reverts to *n*-butyraldehyde rapidly. It is suggested that this polymer is similar to the well-known polymers of formaldehyde but that the energy relationships are such that the polymer is stable only at high pressures.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT OHIO STATE UNIVERSITY]
NATURAL AND SYNTHETIC RUBBER. IV. 4-METHYL-4-OCTENE BY ISOPRENE ETHYLATION

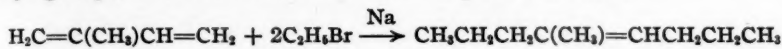
BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

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In preceding papers¹ it has been shown that when isoprene accepts hydrogen, or when two molecules of isoprene link together, the reaction affects only the 1- and 4-positions. This behavior has been regarded as a general property, and it has been used to explain the polymerization of isoprene to synthetic rubber.

The present paper offers one more evidence of the 1,4-addition. Two ethyl groups have been attached to an isoprene molecule



The experimental conditions were precisely those which are required for the formation of synthetic rubber: the reaction took place at room temperature in the presence of an alkaline metal and, in each case, a certain amount of synthetic rubber was formed. This favors the view that the ethylation of isoprene is a process very analogous to its polymerization.

As was expected, the ethyl groups linked exclusively to the first and the fourth carbon atoms; a hydrocarbon was thus obtained which on examination proved to be 4-methyl-4-octene. The criteria used for its identification were a combustion, a molecular weight determination by freezing point depression in benzene, a double bond determination by hydrogenation and by bromination, a computation of the molecular refraction and finally an oxidation with ozone.

Since the experimental results support the postulation that isoprene accepts radicals *exclusively* on its 1- and 4-carbon atoms (under the conditions required for synthetic rubber formation), they also fortify the hypothesis that the chain formula of natural rubber proposed by Staudinger² and his associates is much more acceptable than any formula involving the formation of a ring.

Experimental

Two-gram molecules of metallic potassium are covered with one-gram molecule of isoprene, which has been sufficiently purified to be capable of rapid polymerization. Two-gram molecules of ethyl bromide (or one-gram molecule of ethyl sulfate) is dissolved in a like volume of dry ether, and added gradually to the isoprene. A gentle shaking is maintained, and heat is applied sufficiently to maintain a moderate ebullition. Much gas is evolved; the decomposition of the ethylation agent is the predominant reaction. After twenty-four hours, the residual metal is eliminated by the cautious

¹ Midgley and Henne, *Jour. Am. Chem. Soc.*, **51**, 1215, 1293, 1294 (1929).

² Staudinger and co-workers, *Helv. Chim. Acta*, **5**, 785 (1922), and later papers.

addition of alcohol, and the ethylate is then decomposed with water. The mixture is washed with dilute hydrochloric acid and water, decanted, dried and fractionated. About 4% of the theoretical amount of C_9H_{18} is obtained. This compound shows the following physical constants: b. p. 136–144° (chiefly 139°), d_{20}^{20} 0.7495, n_D^{20} 1.4228, $\Delta = 1.0$ per C_9H_{18} . The molecular weight determined by freezing point depression in benzene was found to be 122: theory requires 126, but the discrepancy is within the permissible experimental error of 3%. A combustion checked the formula already evident. The molecular refraction computed from the density and the refractive index by means of the Lorentz-Lorenz formula was found to be 42.8. This value compares favorably with the theoretical value 43.3.

To prove that isoprene had accepted the ethyl groups exclusively on the 1- and 4-carbon atoms, it was necessary to locate the double bond in the resulting nonene, and this was done by ozone oxidation in a glacial acetic acid solution. The ozonization procedure has been previously recommended.³ After decomposition of the ozonide with a dilute potassium dichromate solution, two compounds were isolated and characterized: methyl butyl ketone and butyric acid. No trace of any other compound was detected. The results of the ozonization were in complete agreement with the formula postulated for the nonene.

Summary

Isoprene has been ethylated; 4-methyl-4-octene was formed exclusively. The structure of this nonene is in agreement with the usual behavior of a conjugated double bond system. This type of addition is further evidence in favor of the hypothesis which regards the polymerization of isoprene to synthetic rubber as the formation of long chains of isoprene units linked together by ordinary valences in the 1,4-position.

COLUMBUS, OHIO

³ Henne, *Jour. Am. Chem. Soc.*, **51**, 2676 (1929).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. V. TETRAMETHYLOCTADIENE

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

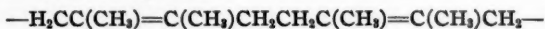
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The third paper of this series¹ has shown how the polymerization of isoprene to synthetic rubber could be stopped at the dimeric stage by addition of an atom of hydrogen to each terminal carbon of the transitory dimer.

A similar experiment can be carried out with dimethylbutadiene substituted for isoprene. Although details differ, the general trend of the reaction remains the same, the reaction products are comparable and the conclusions are similar.

If the views presented before are correct, the linkage of two molecules of dimethylbutadiene, during polymerization to methyl-rubber, should form the transitory compound



Should polymerization be allowed to proceed further, the unstable molecules would link together by their terminal free valences and form a long chain; methyl-rubber would be the final product. This agrees with Kondakow's ideas.² On the other hand, should polymerization be stopped by addition of an atom of hydrogen on each end of the unstable dimeric derivative, a duodecadienic hydrocarbon should result. This hydrocarbon has been isolated and analyzed. As expected, it was 2,3,6,7-tetramethyl-2,6-octadiene.

The polymerization of dimethylbutadiene can never be entirely stopped at the dimeric stage; an appreciable amount of a rubber-like material is always formed. The amount of this compound varies with the experimental conditions. This can be used as an evidence that the formation of tetramethyloctadiene and that of methyl-rubber are simultaneous and analogous processes. Consequently, the structure of the tetramethyloctadiene will have a very close relation to the structure of methyl-rubber. Moreover, since isoprene and dimethylbutadiene behave in a similar way, the structure of ordinary synthetic rubber may be postulated by analogy with that of methyl-rubber.

Experimental

The apparatus, procedure and proportions of reagents have been described previously. Runs were made at 0, 25 and 70°. In each case, 200 g. of dimethylbutadiene

¹ Midgley and Henne, *Jour. Am. Chem. Soc.*, **51**, 1294 (1929).

² I. L. Kondakow, "Scientific Memoirs of the Imperial Yuriev University for the year 1901."

has been used. The best yield was obtained by running at 70°; 65 g. of $C_{12}H_{22}$ was collected and 45 g. of C_8H_{16} recovered, the balance being polymerized to methyl-rubber (15 g.) or carried out with the escaping hydrogen. The tetramethyloctadiene, purified by fractionation under reduced pressure, exhibited the following constants: b. p. (18 mm.) 87.5–88.5°, d_4^{25} 0.7971, n_D^{25} 1.45963. Molecular refraction found, 57.0; calcd., 56.7. The determination of the number of double bonds was made by bromination with a KBr–KBrO₃ mixture, and by hydrogenation in the presence of platinum oxide; in each case 4 atoms were accepted per molecule of hydrocarbon. To complete the analysis, a combustion, a molecular weight determination by freezing point lowering in benzene and an oxidation with ozone were performed. The ozonization was carried out in glacial acetic acid, as reported previously.³ Two compounds were obtained and characterized: acetone and acetylacetone. Not a trace of any other derivative could be detected. The result of the examination thus proves that the formula of the tetramethyloctadiene is $(CH_3)_2C=C(CH_3)CH_2CH_2(CH_3)_2C=C(CH_3)_2$.

The physical constants of the compound obtained by hydrogenation have been measured. They are: b. p. (20–22 mm.) 92°, d_4^{25} 0.7593, n_D^{25} 1.42527; mol. refr. found, 57.2; calcd., 57.6. A combustion and a molecular weight determination agree with the expected values. From its method of formation this compound should be 2,3,6,7-tetramethyloctane.

It is to be noted that when the polymerization is carried out at a low temperature the sample of tetramethyloctadiene obtained is considerably less pure; its boiling point is not constant, it can be fractioned into portions whose densities and refractive indexes vary between d_4^{25} 0.7980 and 0.8003 and n_D^{25} 1.45952 and 1.46111. The odor of the compound strongly resembles that of turpentine. Particularly, the addition of bromine or hydrogen to the double bonds is strongly hampered. This gave the impression that only one double bond was present and led to the erroneous belief that a ring compound had been formed. A better interpretation would be to consider that tetramethyloctadiene formed at low temperature is contaminated by a small quantity of cyclic or even dicyclic compound, which would account for the odor, the higher density and the high refractive index.

Summary

Dimethylbutadiene treated with potassium and alcohol gives 2,3,6,7-tetramethyl-2,6-octadiene and methyl-rubber. The structure of the first hydrocarbon has been established, and is used as an evidence that the methyl-rubber formula must be a long, open chain. This is also regarded as an evidence in favor of the chain formula of natural rubber.

COLUMBUS, OHIO

³ Midgley and Henne, *Jour. Am. Chem. Soc.*, **51**, 2676 (1929).

Cryoscopic Measurements of Rubber Solutions and the Separation of Mixed Phases from Benzene Solutions of Rubber

[9th Communication¹]

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In the case of a large number of natural substances of high molecular weight such as albumin, cellulose, starch, inulin, rubber, and gutta-percha, the size of the molecule is still in dispute, because suitable methods for determining it are lacking and because contradictory results have been obtained by various investigators. The cryoscopic method has been used by most authors, and it has served for the analysis of natural and synthetic substances of high molecular weight.

With rubber and gutta-percha, Staudinger, Asano, Bondy, and Signer² have reexamined the results obtained with camphor and menthol solutions in our earlier work, and they believe that the results can be explained in another manner. In both of the first sections of this work we disprove these experiments, where for the menthol measurements a Beckmann vessel surrounded by a Dewar jacket was used. In the third section observations on rubber solutions in benzene are described, which are of general interest in the cryoscopic investigation of high molecular substances, which perhaps explain contradictions, and which show how this method is applicable only to colloid systems.

1. Experiments in Camphor According to Rast (Work done by A. Andriessen and W. Gündel)

Staudinger has raised three objections against the authenticity of our molecular weight determinations of rubber and gutta-percha according to Rast, which are opposed to his macromolecular conception.

(a) At 180° rubber was already cracked. This is disproved by our proof that the values obtained for a 5-60-min. period of fusion remained constant, a determination which Staudinger (*loc. cit.*) recently confirmed for a 20-hour period of fusion. Therefore the cracking must be complete after 5 min., which is highly improbable.

(b) It is a peculiar characteristic of high molecular hydrocarbons like rubber and gutta-percha that they decompose camphor catalytically. It was disproved by our experiments at increasing concentrations, where both rubber and gutta-percha have given approximately the same values as were to be expected stoichiometrically.

(c) According to the latest work of the authors referred to above, impurities containing oxygen in rubber, and which are themselves decomposed at the beginning of the camphor fusion, should be the cause of the depression. This explana-

tion is supported by sublimation experiments, in which the camphor solidified after fusion, and was sublimed at 0.1 mm. and 100° into a receptacle cooled to -70°. Therefore low decomposition products should also pass over, which should be recognizable by the depressed melting point of the sublimed camphor. The maximum melting point depression found amounted however only to 1.4°, whereas in molecular weight determinations depressions of 5-10° were easily obtained. Actually, however, the depressions of 1.4° of Staudinger stated above were not at any time reproducible with pure rubber, as was established by the author in numerous experiments with various rubber preparations.

The names of the observers for the individual experiments are designated by letters. The work was carried out in a T-tube exactly in accordance with the directions given by Staudinger. First, according to our method of evaporation of the solution in the tube, a rubber film was produced;³ this was dried 6-48 hrs. at 30-40° in a high vacuum, then the 10-fold camphor mixture was very cautiously added by means of a long funnel so that no camphor reached the point of fusion and was then exhausted to 0.02 mm. and fused. It was then placed in an oil bath at 185° and usually in 5-10 min. the rubber dissolved in the camphor (in a few cases it was fused one hour, since Staudinger did not indicate the time of fusion). Then the camphor was sublimed away at 100° by a current of steam directed on the vessel for 1-2 hrs., although even after 10 min. nearly all had passed over; 99.5% of the camphor was recovered. After removal of the fusion mixtures, 5-8 samples were taken and, together with the tube of the original camphor or sublimed camphor, tested in the melting point apparatus. In this manner alkali latex sol (Fraction 2), crepe sol (Fraction 2), alkali-purified total rubber, and gutta-percha were tested. A 0.2° depression of the sublimed camphor was found only with two samples of an old total rubber. Here too the average of the samples remained unchanged, and not infrequently the sublimed camphor fused at 0.1° above the original camphor. An alkali-purified total rubber was also studied. This was prepared in Leverkusen according to my method, and for which I here thank Professor Lecher heartily. The thermometer used was divided into 1/5 degrees.

Preparation Used Observer ()	Camphor in G.	Substance in G.	Per cent. Content of Camphor Solution	Melting Point of Camphor	Sublimed Camphor	Fusion Time, Min.
Alkali latex sol Fraction 2						
(A)	0.0755	0.0068	8.9	179.6°	179.6°	5
(A)	0.1632	0.0137	8.4	179.7°	179.7°	16
Crepe sol Fraction 2						
(G)	0.1184	0.0103	8.7	179.6°	179.6°	7
(G)	0.109	0.0097	9	179.6°	179.6°	60
(A)	0.1293	0.0150	11.6	179.6°	179.6°	5
Alkali total rubber, old						
(G)	0.1248	0.0107	8.6	179.6°	179.6°	9
(G)	0.1162	0.0104	9	179.6°	179.6°	60
Gutta-percha (A)	0.1515	0.0147	9.7	179.6°	179.6°	5
Alkali total (A)	1.5134	0.1522	10	176.9°	176.9°	5
Rubber Leverkusen (A)	1.5261	0.1505	9.9	176.9°	176.9°*	16

* Another thermometer was used here.

II. Determination in Menthol

(Work done by W. Gündel)

The molecular weight determinations in menthol by Staudinger and Bondy show retardation of crystallization which has never been observed by us. These authors have also repeated our experiments with another material (total rubber). We

had used only sol-rubber or reprecipitated gel-rubber, in other words, relatively easily soluble products. Staudinger and Bondy do not state how much nitrogen⁴ and how much ash their total rubber still contained. This material is not well suited for precise experiments. The precautions stated by them, especially the exact standardization of the cooling bath at 0.2° below the freezing point of the solution, the inoculation, etc., had likewise been carefully followed by us and communicated to Staudinger as well. Only in our case the cooling bath was surrounded with an asbestos insulating jacket, having a double window for inspection, and agitated not by air but by means of a propeller. The temperature of the bath must be maintained constant within 0.1° .

The authors mentioned believe that the retardation in the crystallization of menthol by the dissolved rubber vitiates the results and makes them valueless. In one case they obtained a molecular weight of 130 in a 0.45% solution, which is completely out of range. This has not happened in our work, but we have already mentioned explicitly that with 0.5% concentration the method is too inaccurate and gives extremely variable values.⁵ The remaining experiments of Staudinger and Bondy by no means prove that the influence of the retardation in crystallization is so significant as they believe. In Experiment I (1.5% solution) in spite of a difference of 7 minutes in the standardization I, 2, I, 3, the same values (750) were found, with an intermediate retardation point of 950. In Experiments II (3.5% solution) and IV (3.9% solution) the values 980 and 1110 were obtained, although in the first case an average of 25 min. and in the second an average of 60 min. retardation in crystallization compared to the blank experiment were found. Staudinger's best experiment shows a retardation of 21 min. If the most dilute solution (below 1.5%) is excluded, the measurements of Staudinger and Bondy agree satisfactorily with our own.

Nevertheless, we considered it necessary to test the influence of the retardation in crystallization in a more suitable apparatus, and with this object in view the molecular weight vessel was surrounded⁶ by a Dewar jacket, according to a suggestion by Günther Scheibe. In this way the heat loss in the fusion bath was reduced in an extraordinary way. The heating and cooling of the menthol fusion was effected by a gold plated silver plunger, which led in through the rubber stopper, and which for the heating was fed with water at 50° and for the cooling with water at 40° . It was cooled only until the temperature of crystallization was reached. In addition, the Dewar jacket was placed in a hot bath at the crystallization temperature of the menthol solution. Some heat still flowed upward through the platinum stirrer and thermometer.

With this apparatus values for azobenzene of 155–170 (calculated 182) were obtained in about 2 hours of crystallization. With rubber it was possible to have the time of crystallization of the rubber menthol solution intermediate between the time of the blank experiment without rubber or just the same as the latter time. Sol-rubber did not essentially retard the crystallization of menthol, the time of crystallization of the rubber solution being 25–110 min. Two measurements were made of a one per cent. rubber solution, one (menthol of Schimmel & Co.) gave the values of 1170 and 1295, the other (menthol of Riedel) values of 820 and 1080. These are higher values than we had found previously with the one per cent. solution and about the same values which Staudinger and we, in agreement with one another, had found when working with somewhat more concentrated solutions. The still lower values of 5–600, which we found previously with the one per cent. solution and which indicated 8 isoprene residues, no longer appeared under the changed experimental conditions. Rather are the values obtained in menthol of very similar magnitude to those in camphor and those

with hydro-rubber, which indicate 16-24 isoprene groups. We have also found lower values (326, 277) with cholesterol without observing a retardation of crystallization. The uncertainty and the great variations in the values must be due to other causes. The very different quantity of menthol which crystallized out is surprising. Perhaps solvate formation also plays a part here (see Benzene, III). By means of a special experiment we have become convinced that the menthol sublimed from the fusion *in vacuo* showed exactly the correct melting point. It should also be kept in mind that the menthol method can be used also as a fusion method according to Rast, in which case the rate of crystallization plays no part. In this case concentrated solutions must be made and values of 1500-2300⁷ are obtained. Therefore the concentration here affects the measured particle size. Since in other solvents, *e. g.*, camphor and benzene, there is no such dependence, Staudinger concludes that association does not play any part. This conclusion is not convincing, for benzoic acid is dissolved dimolecularly in benzene even at the highest dilutions which allow cryoscopic measurements, and carbon tetrachloride shows a 4-fold molecular weight⁸ in acetone, a further proof of association, even in quite simple systems. It should also be noted here that, according to Karrer and Widmer, perhydrolycopin gives too high a molecular weight (830) in camphor or bromoform, therefore it is associated in spite of its saturated character, while the value in benzene is 525⁹ (calculated 536).

(a) Determination of the Molecular Weight of Sol-Rubber (Crepe Fraction 2) in Menthol.

External Bath, 43.2°; Weight of Menthol, 29.24 g.

	Thermometer Reading	Time, Min.
Inoculation	3.020°	0
Supercooling	2.410°	70
Highest state	2.570°	120
Inoculation	3.020°	0
Supercooling	2.310°	35
Highest state	2.580°	70
Inoculation	3.020°	0
Supercooling	2.350°	85
Highest state	2.580°	130

Weight of rubber, 0.3002 g. after 18 hours' solution at 50°.

Inoculation	2.800°	0
Supercooling	2.292°	45
Highest state	2.472°	90

Depression: 0.108°. $M = 1170$

After 50 hours' solution at 50°

Inoculation	2.900°	0
Supercooling	2.232°	40
Highest state	2.482°	85

Depression: 0.098°. $M = 1295$

(b) Determination of the Molecular Weight of Sol-Rubber (Crepe Fraction 2) in Menthol.

External Bath 42.8°; Weight of Menthol 29.47 g.

	Thermometer Reading	Time, Min.
Inoculation	3.020°	0
Supercooling	2.02°	45
Highest state	2.580°	90

	Thermometer Reading	Time, Min.
Inoculation	3.020°	0
Supercooling	2.22°	55
Highest state	2.572°	115
Inoculation	3.020°	0
Supercooling	2.27°	55
Highest state	2.580°	110

Weight of rubber, 0.3029 g. after 12 hours' solution at 50°

	Thermometer Reading	Time, Min.
Inoculation	3.000°	0
Supercooling	2.180°	55
Highest state	2.425°	90

Depression: 0.155°, $M = 820$

After 38 hours' solution at 50°

Inoculation	3.000°	0
Supercooling	2.211°	55
Highest state	2.460°	110

Depression: 0.118°. $M = 1080$

III. Determinations in Benzene

(Work carried out by A. Andreissen)

We have recently made cryoscopic measurements of three different sol-rubbers in benzene solution and have found that here, too, depressions occur. These vary so much that we are not willing to give the individual experiments (limits of 1500 and 8000 of the molecular weight). It is not necessary to boil rubber in xylene 14 days, as Staudinger and Bondy did, in order to find measurable depressions.

In our determinations we were surprised to find that frozen out benzene varied greatly in its habitus; in many cases there were the ordinary aggregates of hexagons in the form of honeycombs, but many times there were feathery ramified crystalline forms. In the case of the separation of the latter,¹⁰ it again happened that no supercooling with subsequent maximum point appeared, but instead the temperature dropped very slowly, without any particular point appearing. This phenomenon varied from the normal behavior. Since, besides, the calculated molecular weights were at variance with the measurements of the height of climb, which gave a calculated particle size of 200,000, we examined what actually separated out of the benzene solution. As a result it was evident that it was not pure benzene, but a mixed phase of benzene and rubber which frequently showed almost the identical rubber content as the original solution. Since the crystals were deposited firmly on the wall of the vessel, which was stirred with a platinum rod, it was possible to pour off the mother liquor. It must not be assumed that such a large quantity of rubber remained with the crystals by adhesion of the mother liquor. The difference in concentration between the crystals and the mother liquor was much too small.

The following experiments were carried out:

- (a) 0.2700 g. rubber in 27.9847 g. benzene (0.955% solution).
Separated crystals: 2.6185 g., containing 0.0209 g. of rubber (0.80% solution).

From the mother liquor poured off from the crystals 23.6124 g., containing 0.2403 g. of rubber (1.02% concentration).

- (b) 0.8152 g. of rubber in 81.6819 g. of benzene (0.99% solution).
Separated crystals 29.4814 g., containing 0.2505 g. of rubber.

49.5848 g. of mother liquor poured off, containing 0.55378 g. of rubber, (1.15%).

Here one part of rubber should be retained by 100 parts of benzene in the solvate. This we do not consider a stoichiometric relation.

- (c) 0.5347 g. of rubber (alkali-purified latex, Fraction 2) in 48.2304 g. benzene (1.09% solution).

Separated crystals 15.6660 g., containing 0.1696 g. of rubber (1.08% solution).

- (d) Original solution 0.5%, crystals 0.7%.¹¹

- (e) Original solution 1.0%, crystals 1.03%.

- (f) Original solution 1.64%, crystals 1.68%.

- (g) Original solution 0.51%, crystals 0.48%.

The crystals which separated from the rubber-benzene solutions often showed therefore almost the same rubber content as the original solution, though occasional fluctuations above or below appeared. For the depressions to be of any value as molecular weight determinations it would have to be assumed that the pure solution medium crystallized out. Because this was not the case here, we were not able to make use of the values obtained from these solutions without falling into error.

The situation was somewhat mitigated by the fact that crystals and mother liquor had nearly the same composition, therefore perhaps the rubber was not able, owing to the strong solvation, to diffuse out of the crystallized range of the solution. Moreover, it is noteworthy that no depressions were found^{11a} with raw and total rubber.

If the depressions really originated from dissolved particles of the size of 2-8000, they should be evident in the height of climb of this solution, which was not the case. Moreover, with menthol solutions of rubber, as similar experiments carried out in the I.-G. Farbenindustrie Ludwigshafen (Fikentscher) and in our laboratory (H. Kroeplin) have shown, no climbs were observed which would lead to cryoscopically measured particle sizes of 1200, but rather to much smaller ones.

Establishment of the fact that mixed phases of rubber and solutions can crystallize out offers a possible explanation for this contradiction and is of some significance in our opinion, not only for rubber, but for many other investigations of high molecular substances, such as albumin, cellulose, inulin, and the like. Certainly one is not going to consider misleading all cryoscopic results on the basis of a few measurements of sol-rubber. However, according to the foregoing facts, cryoscopic measurement of colloidal systems can at best be evaluated in the determination of molecular weights only if it is proved that pure solvent crystallizes out or if the above sources of error are better understood than is possible today. Until now this point has received too little attention. At any rate, we must respect Meyer and Mark¹² when they mistrust the application of the cryoscopic method in colloidal systems.

Their rejection of the cryoscopic method "because on the one hand strong retardation of the freezing influences the result and on the other hand because even small quantities of low molecular substances can vitiate the results" is more applicable in the case of rubber. The essential factor is solvation, likewise mentioned by these authors. The retardation of freezing, which Staudinger emphasizes especially, we were able to show as unessential in the case of sol-rubber by the use of our cryoscopic Dewar apparatus. But this does not necessarily mean that with other materials (cyclo-rubber¹³) it does not perhaps play an important role. In regard to the impurities, there is less difficulty with a hydrocarbon like rubber than with carbohydrates or proteins, for, in order to make an error of about 1000 in a substance of infinite molecular weight, the impurities would have to be present

in considerable quantities. Accordingly with 1000 grams of rubber, 1 gram-mol. of impurity would have to be present, or in per cent., $1/10$ gram-mol., for example: 1.8% water, 7.4% ether, 6.8% isoprene, 13.6% limonene, 27.2% of a diterpene, etc. This is readily excluded by analysis. Only with experimental values of particle sizes of 4-5000 can the depression be regarded as influenced by impurities in the rubber.

However, in the other particular, we agree completely with Meyer and Mark, that the solvation of the rubber molecule is very great. Therefore the free available quantity of solvent is less than appears from the weight. The cryoscopically determined particle size must therefore appear too low. How great the error is, and whether it can be corrected, is still uncertain.

Summary

We consider the separation of mixed phases in cryoscopic investigations of colloidal systems and of rubber mixtures in particular as a dangerous source of error. Therefore we place no importance on the great variations in the depressions which occur with sol-rubber in benzene. The menthol values vary less, but nevertheless more than usual. The depressions of camphor fusions proceeded strictly stoichiometrically and led to almost the same value (about 1200) as the cryoscopic menthol measurements. In both the latter instances the composition (rubber content) of the crystallized phase has not yet been studied, since the experimental difficulties involved in the separation of the crystals from the viscous fusion liquid have not yet been overcome.

References

- ¹ *Ber.*, **61**, 1583, 1591 (1928); *Z. angew. Chem.*, **42**, 74 (1929); *Kautschuk*, **5**, 129.
- ² *Ber.*, **61**, 2575 (1928).
- ³ With total rubber, small pieces were added, allowed to swell in a little ether overnight, and then evaporated.
- ⁴ The carbon-hydrogen determination without a reduced copper spiral proves nothing about the purity. Cf. *Ber.*, **61**, 1584 (1928).
- ⁵ *Ber.*, **60**, 2174, Note 17 (1927). This is not mentioned by Staudinger.
- ⁶ The vessel was manufactured by R. Goertz, Leipzig, the plunger by Heraeus, Hanau.
- ⁷ *Ber.*, **60**, 2173 (1927); Hock and Fromandi, *Kolloidchem. Beihefte*, **27**, 189 (1928).
- ⁸ Felger, *Diss. Erlangen*, 1926, 59.
- ⁹ *Helv. chim. acta*, **11**, 151 (1928).
- ¹⁰ This was also observed occasionally in pure benzene.
- ¹¹ This is the only experiment in which the concentration of the rubber in the crystals exceeded to any marked degree that in the original solution. The control experiment resulted otherwise. Experiments *a* and *b* used crepe sol, those from *c* to *g* used latex sol.
- ^{11a} Staudinger and Bondy, *Ann.*, **468**, 36 (1929).
- ¹² *Ber.*, **61**, 1946 (1928).
- ¹³ With cyclo-rubber, which gave a value of 8500 in benzene, Staudinger found a value of 150 in menthol, values which naturally are limited by any errors in the method (retardation of crystallization or separation of mixed phases). He considers the benzene value of 8500 to be correct, "since the point of liquefaction, the solubility, and the viscosity of the solution indicate this average molecular weight." Cyclo-rubber is a highly complicated mixture, and it is known that all three of the properties mentioned above are greatly influenced by impurities, so that such a conclusion seems hardly possible. Moreover, the separation of mixed phases lies within the realm of possibility. We have not investigated cyclo-rubber.

Isoprene and Rubber

XIII.¹ The Constitution of Rubber

H. Staudinger, M. Asano, H. F. Bondy, and R. Signer

It is of special interest in connection with the structure of rubber as well as that of all natural products of high molecular weight that two basically different viewpoints exist, and that both have been supported by experimental investigations. Both these concepts concerning the constitution of rubber are discussed in the following paper.

I. The Constitution of Rubber According to Pummerer²

Pummerer defends the correctness of the basic concept of Harries "that a parent rubber hydrocarbon exists, which as a result of some condition tends to association and as a result gives the impression of a rubber of gigantic molecular weight. The question of whether this point of view is justified is of the greatest interest to colloid chemistry. The tendency to association may depend upon various factors, for example, upon the state of saturation, upon the size, or even upon the form of the molecules."³

Pummerer expresses similar ideas, as does Bergmann⁴ about the constitution of polysaccharides and albumins. This concept is supported by Pummerer by important experiments.

1. By sufficient purification, Pummerer and Koch⁵ were able to obtain a crystallized rubber, and they consider it improbable that the parent rubber molecule is extraordinarily large and contains several hundred carbon atoms. They are led to this from a concept that only unitary simple molecules can form crystals. They believe that they have obtained such a simple rubber through their method of purification.

2. By means of hydrogenation of rubber in the cold, Pummerer and Koch⁶ obtained a hydro-rubber which could be distilled without decomposition, and which gave a molecular weight of 600-700. Consequently the parent hydrocarbon substance must consist of from 8 to 10 isoprene molecules.

3. The molecular weight determinations of Pummerer, Nielsen, and Gündel⁷ are a confirmation of this idea. According to Pummerer, an ordinary solvent such as benzene cannot overcome the association of the parent molecules in the colloid particle. In camphor and particularly in menthol, he believes he has found the solvent which dissolves the parent molecule in a monomolecular state or only slightly associated, for on the basis of molecular weight determinations in dilute menthol solutions the parent hydrocarbon should consist of 8 isoprenes (mol. wt., 544). The values obtained vary from 513 to 1317. In camphor also, the purified rubber value was between 1050 and 1580, which points to a parent molecule of relatively low molecular weight.

4. These data are confirmed by molecular weight determinations of iso-rubber nitrone by Pummerer and Gündel.⁸

5. According to the x-ray measurements of Hauser and Mark⁹ on stretched rubber, the crystallized rubber component should have an isoprene number which is divisible by 4. Pummerer sees in this a confirmation of his theory that the parent molecule contains 8 isoprene residues.¹⁰ According to Ott, the x-ray

diagrams indicate a rubber molecule of $[C_5H_8]_6$. Ott says: "the idea of a very high degree of polymerization is no longer tenable in rubber chemistry."

Although we have another point of view regarding the constitution of high molecular weight compounds, which is based on experimental investigations of synthetic products such as polysterols, these points are very important to Pummerer and his collaborators, and suggest the conjecture that in the natural substances concerned, another principle of synthesis rules from that with synthetic compounds. Even observations on synthetic products might serve to support this concept.

(a) Thus one of us with Felix and Geiger¹³ obtained addition products of dimethylketene and isocyanate and carbon disulfide which showed the properties of high molecular substances, while almost similar complex addition products of dimethylketene and carbon dioxide were crystallized and dissolved in a low molecular state.

COMPOSITION OF THE DIMETHYLKETENE DERIVATIVES

Crystalline, normal solubility	O : C : O	2 mol. ketene + 1 mol. CO ₂ ; 3 mol. ketene + 2 mol. CO ₂ ; 4 mol. ketene + 3 mol. CO ₂
Amorphous, colloid-soluble	{	O : C : N. C ₆ H ₅ 2 mol. ketene + 3 mol. isocyanate; 1 mol. ketene + 4 mol. isocyanate
		O : C : N. C ₁₀ H ₇ 3 mol. ketene + 2 mol. isocyanate
		O : C : N. C ₆ H ₄ . NO ₂ 3 mol. ketene + 2 mol. isocyanate
		O : C : S 5 mol. ketene + 2 mol. COS
		S : C : S 5 mol. ketene + 2 mol. CS ₂

The similarity in the composition of the various substances at once raised the question whether the colloid solubility of the products was not the result of association which originated from the complicated structure, for the molecular weight which was determined through chemical studies of the composition was much smaller than that determined by the osmotic method. This led to the conclusion that with colloid-ketene addition products, as well as with polysaccharides and albuminous substances, it might be possible to obtain a relatively simple parent molecule, the transformation of which to the colloid molecule has until now not been established beyond question.

(b) In the polymerization of cyclopentadiene,¹⁴ an insoluble polymerization product was obtained along with the dimeric, trimeric, tetrameric, and pentameric soluble polymerization products. Its molecular weight, based on a comparison with the other polymers, was $[C_5H_8]_6$. This is therefore relatively low, although the compound has the character of a high molecular substance.

(c) With the alkali salts of fatty acids, the normal solubility in water decreases from a definite molecular size on, and colloid particles are formed. Though a homopolar hydrocarbon should not be compared with heteropolar salts as far as solubility is concerned (this will be discussed elsewhere), still it may be concluded from this comparison that also in the case of a hydrocarbon below a definite molecular weight rather sudden anomalous properties, for example anomalous solubility, might appear.

II. Constitution of Rubber According to H. Staudinger

The view has already been held that rubber has a high molecular weight and is a polyprene.¹⁵ This idea was taken up by Staudinger; however, he expanded it so that it concerned not a uniform high molecular hydrocarbon but a mixture of hundreds of polymeric homologous polyprènes which are distinguished by the degrees of polymerization.¹⁶ A separation of such a mixture by distillation is in-

conceivable, since the boiling point of such a hydrocarbon is considerably above the decomposition point.¹⁷

In spite of the investigations of Pummerer this idea was well supported, and since Pummerer considers it unproved,¹⁸ a few fundamental arguments are again presented here.¹⁹

1. The hydrogenation of rubber leads to a mixture of high molecular paraffin hydrocarbons.²⁰ Since under the conditions of hydrogenation, especially at higher temperatures, decomposition (cracking) rather than an upbuilding of hydrocarbon chains ensues, rubber must itself be of high molecular weight.

2. In reactions of rubber in which the molecule is not broken down, colloid-soluble derivatives of high molecular weight are obtained. Thus ethyl hydro-rubber, which is obtained from rubber halides with zinc diethyl, is a high molecular hydrocarbon.²¹

3. In the polymerization of sterol in the cold, a polysterol is formed. According to our concept this has a similar structure to rubber, since, like rubber, it forms colloid solutions and is elastic when warm.²² It may be shown that this polysterol has an average molecular weight far above 10,000. It is not likely that the structural principles of two products which are so similar should be different.

4. The colloid particles of rubber, like polysterol solutions, cannot form associations of small molecules. On heating such solutions the viscosity diminishes and is in fact irreversible. The phenomenon must therefore depend upon a diminution in the size of the molecule, *i. e.*, the long hydrocarbon chains are cracked. If it were an association, the process would have to be reversible.

III. Discussion of the Idea of Pummerer

Both concepts of the structure of rubber are irreconcilably opposed to one another. We have therefore examined the observations of Pummerer, and it will be shown in the following sections how they may be explained.

1. The crystallization of a compound is no argument that it is simple and of low molecular weight, for the mixture of polymeric homologous polyoxymethylenes crystallizes as sharply as simple low molecular polyoxymethylene diacetate by means of a parallel arrangement of the chains.²³ Only in this case no normal molecular lattices can form. These crystallized structures, which give a Debye-Scherrer diagram, possess a macromolecular lattice and have a fibrous structure, yet they do not consist of simple long molecules. They are "crystallites" and are identical with the micelles of Nägelis.²⁵

2. According to our observation, there does not exist an undecomposed distillable hydro-rubber of the composition $[C_8H_{10}]_n$. In the distillation of the hydro-rubber, which has a much higher average molecular weight (3000-5000), cracking occurs, with the formation of unsaturated hydrocarbons.²⁶

3a. The molecular weight determinations of rubber in menthol were tested, with the result that in this extraordinarily slowly crystallizing solvent only high molecular weight determinations can be carried out, as has already been observed by Garelli and Calzolari.²⁷ Molecular weight determinations can be carried out only if after addition of the substance, the crystallization proceeds about as rapidly as in the pure solvent, and if at the same time care is taken that the external temperature remains constant. By the addition of rubber, on the contrary, the rate of crystallization is retarded to an extraordinary degree. After supercooling, at the commencement of crystallization, a more or less considerable quantity of heat flows off into the surrounding cooling bath. Depressions varying greatly are obtained in consequence and, according to the working conditions, the most varied values for the molecular weight of rubber are obtained.

We made similar experiments on the molecular weight determination of a cyclo-rubber which had an average molecular weight in benzene of 8500. We consider the latter value correct in its general order of magnitude, since the liquefying point, the solubility, and viscosity of the solution indicate this average molecular weight, and a comparison with other cyclo-rubbers with different average molecular weights is possible.²⁸ In menthol a molecular weight of 150 was obtained, which does not agree with the properties of this product.

3b. The molecular weight determinations in camphor gave the following results: It was established, with the aid of high molecular paraffin hydrocarbons and paraffin hydrocarbon mixtures, that the Rast method is suited to the determination of the molecular weight of high molecular stable hydrocarbons and mixtures. The results obtained with rubber by Pummerer, Nielsen, and Gündel were confirmed in their essentials. Thus the molecular weight values varied between 1000 and 2000. However, at high temperatures slight decomposition took place, for the super-sublimed camphor showed a lower melting point than the sublimed pure camphor. It must have been contaminated, therefore, by low molecular weight decomposition products.²⁹ According to our observations, these originated in impurities containing oxygen in the rubber or gutta-percha, which are decomposed on heating to 150° with the evolution of volatile compounds. The weight of wholly pure rubber, on the contrary, does not alter on heating to 150° *in vacuo*.

Further proof that the molecular weight determinations of these unsaturated high molecular substances in camphor do not give correct values may be seen in the fact that cyclo-rubbers, whose molecular weights in benzene agree with their physical properties such as their melting point, solubility, and viscosity of solution, give in camphor essentially lower values. In molecular weight determinations in benzene we consider association as non-existent, since the same values were obtained at various concentrations. When these cyclo-rubbers were isolated again after their solution in camphor, and their molecular weight in benzene determined, the original values were again obtained. Furthermore, the viscosity of the benzene solutions of both these cyclo-rubbers underwent no change through their solution in melted camphor. Moreover cyclo-rubber is autooxidizable and an autooxidized product gives off volatile substances when heated to 150° *in vacuo*. The greater part of the product remains unaltered, and consequently the same average molecular weight is obtained in benzene even after solution of the substance in camphor and recovery from this, for the small quantities of decomposition products remain dissolved in the alcohol.^{29a}

3c. Pummerer's belief that menthol and camphor are particularly good solvents for rubber in contrast to benzene, dipentene, and isoprene which form colloid solutions, appears to us improbable, for, as is known, a substance dissolves much more easily in a closely related solvent than in one belonging to another group. As has already been proved, this applies to the high molecular products, eucoloids.³⁰ The rubber hydrocarbon should dissolve best in hydrocarbons, and on the contrary with greater difficulty in an alcohol like menthol.

3d. Inconclusive are the views of Meyer and Mark³¹ that "under the influence of certain solvents the rubber micelles break up either into small aggregates of primary valence chains or into primary valence chains themselves. From this point of view rubber occupies an intermediate position between soap solutions whose micelles are in a permanent equilibrium with free fatty acid molecules, and cellulose or starch where the micelles cannot be split up in a reversible manner by any kind of a solvent." The colloid particles of a soap solution, which are termed micelles, are quite differently constructed from the colloid particles of a

rubber solution. There we have electrically charged colloid particles and the charges are of importance in governing the state of the micelle. Rubber is a homopolar compound: its solution contains macromolecules which naturally, considering their great size, are highly solvated and therefore give a high viscosity to the solution.³² The idea of both authors, that various solvents can decompose the micelle union in different ways, is not tenable according to the foregoing experiments.

4. Iso-rubber nitron is not, as Pummerer assumes, a simple substance, but is a mixture of polymeric homologous products, which are formed through decomposition of the rubber with nitrosobenzene. Such a decomposition of the rubber hydrocarbon is brought about by the action of oxidizing agents. This will be reported in a following paper.

5. X-ray investigations do not prove the existence of a small parent molecule, for the small elementary cell permits of no conclusions regarding the molecular size in the case of high polymers. According to the investigations by Mie and Hengstenberg³³ the molecule in the high polymers can be much greater than the elementary cell. One of us has already pointed out this inconclusive argument of Pummerer.³⁴ In more recent times, Meyer has repeated this determination.³⁵

Closing Remarks

According to the foregoing, the experiments presented by Pummerer as a basis for his theory of the constitution of rubber are not convincing. Therefore we adhere to our idea and regard rubber as consisting of macromolecular polymeric homologous polyprenes.

Description of the Experiments

I. The Determination of Molecular Weights in Menthol³⁶ (H. F. Bondy)

1. *Apparatus.*—As a supercooling bath we used a 2.5 l. beaker filled with water. In the beaker was a toluene-thermoregulator. In order to agitate the bath thoroughly, a continuous stream of air was led through. In this way it was possible to maintain the temperature of the bath constant to about 0.2°.

2. *Execution of the Determinations.*—The determinations were carried out in a Beckmann apparatus with a ground-in thermometer which permitted reading to 0.001°. In order to melt the menthol³⁷ and to produce the menthol solution, the Beckmann apparatus, together with the thermometer, was placed in a cabinet having a constant temperature of 50°. After the menthol had been fused, the apparatus was placed in the cooling bath described above. At the melting point inoculation was made with a few menthol crystals, the temperature and time being noted. Furthermore, the time when the onset of crystallization was manifest was noted. When the lowest point of the thermometer was reached the temperature and time were again taken. From time to time the temperature and time were read until the maximum point was reached. Each determination was carried out three to four times in this way. The average value was then taken as the correct melting point. A few determinations of low and high molecular substances are given in the following.

3. *Determination of the Melting Point of Pure Menthol at Various Temperatures of the Supercooling Bath.*—Menthol—initial weight—20.46 g. The crystallization of the menthol proceeded very slowly as a result of the high viscosity, so that the influence of the supercooling bath is very great. In a determination in benzene the crystallization took place rapidly, the thermometer reached equilibrium within 1 min., and the influence of the supercooling bath could therefore be disregarded

if this temperature did not vary too much. In the case of menthol, however, crystallization continued from 15 min. to 2 hrs., according to the temperature of the supercooling bath.

(a) Temperature of the Supercooling Bath: 38° .—At 38° we are about 4° below the melting point of menthol. The influence of the supercooling bath is therefore so great that all the liberated heat of crystallization is given off to the supercooling bath, and an ascent of the thermometer is in general not observed.

(b) Temperature of the Supercooling Bath: 41° .

	Temperature, Degrees	Time, Min.
Inoculation	1.960	0
Beginning of crystallization	1.790	2
Supercooling ^{37a}	1.620	7
	1.730	10
	1.966	16
Highest point	1.971	18
	1.962	20
Inoculation	1.950	0
Beginning of crystallization	1.810	2
Supercooling	1.700	6
Highest point	2.245	24
	2.240	25
Inoculation	1.950	0
Beginning of crystallization	1.830	2
Supercooling	1.619	7
Highest point	2.178	25
Inoculation	2.100	0
Beginning of crystallization	1.990	1
Supercooling	1.775	5
Highest point	2.269	23
Inoculation	2.060	0
Beginning of crystallization	1.960	1
Supercooling	1.729	8
Highest point	2.130	23

The thermometer was read after about 20 min. The values which were obtained in this way were so much at variance that no molecular weight determinations could be made. Therefore we raised the temperature of the supercooling bath.

(c) Temperature of the Supercooling Bath: 42.5° .—This temperature is too near the melting point of menthol. The mercury thread moved only very slowly and then remained almost stationary.

(d) Temperature of the Supercooling Bath: 42.0° .

	Temperature, Degrees	Time, Min.
Inoculation	2.110	0
Beginning of crystallization	2.095	3
Supercooling	2.090	6
	2.109	15
	2.108	18 (fluctuation)
	2.258	45
	2.252	48 (fluctuation)
Highest point	2.380	123

	Temperature, Degrees	Time, Min.
Inoculation	2.300	0
Beginning of crystallization	2.270	1
Supercooling	2.115	15
	2.148	18
	2.142	21 (fluctuation
	2.321	90
	2.251	120
Highest point	2.351	135
	2.280	270
	2.190	The next morning

Here it required too long for the thermometer readings, and consequently variations were obtained in the reading.

(e) Temperature of the supercooling bath: 41.5°.

	Temperature, Degrees	Time, Min.
Inoculation	2.300	0
Beginning of crystallization	2.200	2
Supercooling	1.800	10
Highest point	2.300	69
	2.300	75
Inoculation	2.300	0
Beginning of crystallization	2.220	3
Supercooling	1.800	11
Highest point	2.260	57
	2.260	60
Inoculation	2.230	0
Beginning of crystallization	2.110	3
Supercooling	1.830	12
Highest point	2.289	72
Average	2.283	

If the values obtained for the various temperatures of the supercooling bath are compared, it will be seen that the influence of the supercooling bath is very great since for each temperature other melting points were found.

Summary

Only if the temperature of the supercooling bath was maintained at 41.5° were the values which were obtained of any use. In this case, the temperature of the supercooling bath was about 0.7° below the melting point of menthol. The reading of the thermometer could be carried out in about one-half hour. From the beginning of crystallization to the supercooling point about 8 minutes elapsed. During this time the heat of crystallization passed off into the supercooling bath. We did not therefore obtain the real melting point of menthol, but a point which depended upon the heat of crystallization and the influence of the supercooling bath. Under the best conditions molecular weight determinations in menthol were possible only if the same conditions of crystallization were maintained in the solution as in pure menthol.

4. *Determination of the Molecular Weight of Cetyl Alcohol in Menthol* ($K = 124$).—Cetyl alcohol, original weight: 0.6632 g. Menthol, original weight: 20.46 g. In order to solidify the solution the temperature of the supercooling bath had to be lowered. We chose such a temperature that once more we were about 0.7° below the new melting point in order to have the same conditions as with pure menthol.

Melting point determination of menthol: see 3e. Temperature of the supercooling bath: 40.0°.

	Temperature, Degrees	Time, Min.
Inoculation	0.620	0
Beginning of crystallization	0.500	1
Supercooling	0.305	8
Highest point	0.766	57
$\Delta = 1.517^\circ$ $M = 256$		
Inoculation	0.700	0
Beginning of crystallization	0.550	1
Supercooling	0.492	7
Highest point	0.828	54
$\Delta = 1.455^\circ$ $M = 276$		
Inoculation	0.700	0
Beginning of crystallization	0.495	1
Supercooling	0.350	8
Highest point	0.815	54
$\Delta = 1.468^\circ$ $M = 274$		
$M = 265, 276, 274$		
$M \text{ (calculated)} = 230$		

Here it will be seen that the molecular weight of cetyl alcohols can be determined, although very inaccurately. The rate of crystallization and the time from the beginning of crystallization to the supercooling point were not essentially different from those of pure menthol.

5. *Determination of the Molecular Weight of Cholesterol in Menthol.*—Original weight of menthol: 15.45 g. Temperature of the supercooling bath: 41.5° .

	Temperature, Degrees	Time, Min.
Inoculation	2.300	0
Beginning of crystallization	2.070	4
Supercooling	1.740	10
Highest point	1.560	72
Inoculation	1.900	0
Beginning of crystallization	1.852	4
Supercooling	1.650	10
Highest point	1.962	75
Inoculation	1.900	0
Beginning of crystallization	1.834	4
Supercooling	1.630	10
Highest point	1.982	75
Average	1.970	

Original weight of cholesterol I : 0.2181 g. Temperature of supercooling bath: 40.9° .

	Temperature, Degrees	Time, Min.
Inoculation	1.400	0
Beginning of crystallization	1.295	4
Supercooling	1.150	16
Highest point	1.350	108
$\Delta = 0.620^\circ$ $M = 282$		
Inoculation	1.300	0
Beginning of crystallization	1.201	4
Supercooling	1.170	15
Highest point	1.238	103
$\Delta = 0.732^\circ$ $M = 236$		

	Temperature, Degrees	Time, Min.
Inoculation	1.300	0
Beginning of crystallization	1.195	5
Supercooling	1.180	18
Highest point	1.330	103

$$\Delta = 0.640^\circ \quad M = 274$$

$$M = 282, 236, 274$$

$$M \text{ (calculated)} = 386$$

Original weight of cholesterol I + II: 0.3868 g. Temperature of the supercooling bath: 40.5°.

	Temperature, Degrees	Time, Min.
Inoculation	1.000	0
Beginning of crystallization	0.875	7
Supercooling	0.520	25
Highest point	0.719	94

$$\Delta = 1.251^\circ \quad M = 249$$

Inoculation	0.700	0
Beginning of crystallization	0.685	1
Supercooling	0.592	18
Highest point	0.800	96

$$\Delta = 1.170^\circ \quad M = 265$$

Inoculation	0.700	0
Beginning of crystallization	0.670	2
Supercooling	0.540	19
Highest point	0.950	94

$$\Delta = 1.020^\circ \quad M = 304$$

Inoculation	0.700	0
Beginning of crystallization	0.672	2
Supercooling	0.529	20
Highest point	0.865	103

$$\Delta = 1.105^\circ \quad M = 280$$

$$M = 249, 265, 304, 280$$

$$M \text{ (calculated)} = 386$$

It will be seen that the molecular weight is much too low. This indicates that the conditions of crystallization of the solution are different from those for pure menthol. The entire process continued for about 20 minutes longer than for pure menthol. Therefore the influence of the supercooling bath was felt for a longer period, and as a result the thermometer no longer rose so high. Moreover the time which elapsed between the beginning of crystallization and the supercooling point was, on the average, about 10 minutes greater than for pure menthol. Much more heat of crystallization therefore passed off into the supercooling bath.

6. *Determination of the Molecular Weight of Cyclo-rubber³³ in Menthol.*—Original weight of menthol: 17.20 g. (for Experiment I). Temperature of the supercooling bath: 41.5°.

	Temperature, Degrees	Time, Min.
Inoculation	1.400	0
Beginning of crystallization	1.207	1
Supercooling	1.160	9
Highest point	1.420	54
Inoculation	1.380	0
Beginning of crystallization	1.208	1
Supercooling	1.200	9
Highest point	1.429	54

	Temperature, Degrees	Time, Min.
Inoculation	1.400	0
Beginning of crystallization	1.209	1
Supercooling	1.150	9
Highest point	1.422	57
Average	1.423	

Original weight of cyclo-rubber: 0.2330 g. (for Experiment I). After a few preliminary experiments the best temperature of the supercooling bath was found to be 40.5°.

	Temperature, Degrees	Time, Min.
Inoculation	0.700	0
Beginning of crystallization	0.589	5
Supercooling	0.130	65
Highest point	0.514	108

$\Delta = 0.909^\circ$ $M = 184$

Inoculation	0.700	0
Beginning of crystallization	0.640	1
Supercooling	0.188	40
Highest point	0.410	106

$\Delta = 0.013^\circ$ $M = 166$

Inoculation	0.500	0
Beginning of crystallization	0.321	2
Supercooling	0.100	47
Highest point	0.510	124

$\Delta = 0.913^\circ$ $M = 180$

$M = 180, 166, 184$

M determination in Benzene = 8500, 8100, 8100

M determination in Camphor = 1800, 1900

Original weight of menthol for Determination II: 17.77 g. Temperature of the supercooling bath: 41.5°.

	Temperature, Degrees	Time, Min.
Inoculation	1.200	0
Beginning of crystallization	1.150	1
Supercooling	1.106	8
Highest point	1.145	61

Inoculation	1.200	0
Beginning of crystallization	1.164	1
Supercooling	1.962	10
Highest point	1.190	50

Inoculation	1.200	0
Beginning of crystallization	1.132	3
Supercooling	1.950	10
Highest point	1.080	50

Inoculation	1.130	0
Beginning of crystallization	1.084	2
Supercooling	0.940	10
Highest point	1.222	62

Average 1.142

Original weight of cyclo-rubber for Determination II: 0.2690 g. Temperature of the supercooling bath: 40.7°.

	Temperature, Degrees	Time, Min.
Inoculation	0.520	0
Beginning of crystallization	0.340	5
Supercooling	0.020	26
Highest point	0.516	120

$\Delta = 0.626^\circ$ $M = 300$

	Temperature, Degrees	Time, Min.
Inoculation	0.500	0
Beginning of crystallization	0.412	3
Supercooling	0.306	54
Highest point	0.526	142
$\Delta = 0.616^\circ \quad M = 304$		
Inoculation	0.500	0
Beginning of crystallization	0.402	3
Supercooling	0.148	25
Highest point	0.589	120
$\Delta = 0.553^\circ \quad M = 338$		
$M = 300, 304, 338$		
M determined in Benzol = 6500		
M determined in Camphor = 1500		

The values for cyclo-rubber obtained in both determinations cannot be correct. The values are different from the determination in benzene and also from those in camphor. We consider the values found in benzene correct, because they agree with the properties of the substance. The molecular weight found is also far too low for the same reasons as in the determination of cholesterol.

7. *Determination of the Molecular Weight of Rubber³⁹ in Menthol.*—Original weight of menthol for Experiment I: 17.67 g. Temperature of the supercooling bath: 41.5° .

	Temperature, Degrees	Time, Min.
Inoculation	2.050	0
Beginning of crystallization	2.012	1
Supercooling	1.800	8
Highest point	2.405	56
Inoculation	2.220	0
Beginning of crystallization	2.215	1
Supercooling	1.980	9
Highest point	2.468	51

Two other values were obtained after the same length of time.

Highest point	2.409
Highest point	2.362
Average	2.412

Original weight of rubber (for Expt. I): 0.2708 g.³⁹ (4 days at 50° were necessary for solution). Temperature of the supercooling bath: 41.5° .

	Temperature, Degrees	Time, Min.
Inoculation	2.200	0
Beginning of crystallization	2.020	5
Supercooling	1.875	19
Highest point	2.221	82
$\Delta = 0.191^\circ \quad M = 995$		
Inoculation	2.200	0
Beginning of crystallization	2.125	1
Supercooling	1.940	24
Highest point	2.159	82
$\Delta = 0.253^\circ \quad M = 750$		
Inoculation	2.000	0
Beginning of crystallization	2.110	1
Supercooling	1.765	17
Highest point	2.160	80
$\Delta = 0.252^\circ \quad M = 755$		
$M = 995, 750, 755$		

Original weight of rubber I + II: 0.3883 g. (in solution 4 days at 50°). Temperature of the supercooling bath: 41.3°.

	Temperature, Degrees	Time, Min.
Inoculation	2.000	0
Beginning of crystallization	1.940	1
Supercooling	1.840	11
Highest point	2.135	78

$$\Delta = 0.277^\circ \quad M = 975$$

Inoculation	2.000	0
Beginning of crystallization	1.930	1
Supercooling	1.770	12
Highest point	2.122	73

$$\Delta = 0.290^\circ \quad M = 935$$

Inoculation	2.000	0
Beginning of crystallization	1.930	1
Supercooling	1.773	13
Highest point	2.139	80

$$\Delta = 0.273^\circ \quad M = 994$$

$$M = 975, 935, 994$$

Original weight of menthol for rubber determination III: 18.03 g. Temperature of the supercooling bath: 41.5°.

	Temperature, Degrees	Time, Min.
Inoculation	1.140	0
Beginning of crystallization	1.041	4
Supercooling	1.012	11
Highest point	1.200	59

After the thermometer became stationary the following values were found:

Highest point	1.200
Highest point	1.060
Highest point	1.170
Average	1.158

Original weight of rubber I: 0.0817 g. Temperature of the supercooling bath: 41.5° (in solution for 2 days at 50°).

	Temperature, Degrees	Time, Min.
Inoculation	1.000	0
Beginning of crystallization	0.970	3
Supercooling	0.901	21
Highest point	1.003	114

$$\Delta = 0.155^\circ \quad M = 363$$

Inoculation	1.000	0
Beginning of crystallization	0.965	3
Supercooling	0.950	22
Highest point	1.031	117

$$\Delta = 0.127^\circ \quad M = 435$$

$$M = 363, 435$$

After the solution had stood another 4 days at 50° the melting point was again determined.

	Temperature, Degrees	Time, Min.
Inoculation	1.000	0
Beginning of crystallization	0.879	3
Supercooling	0.604	28
Highest point	0.657	125

$$\Delta = 0.501^\circ \quad M = 112$$

	Temperature, Degrees	Time, Min.
Inoculation	1.000	0
Beginning of crystallization	0.882	4
Supercooling	0.838	46
Highest point	0.872	122
$\Delta = 0.286^\circ$ $M = 193$		
Inoculation	1.000	0
Beginning of crystallization	0.835	5
Supercooling	0.566	29
Highest point	0.765	120
$\Delta = 0.393^\circ$ $M = 141$		
$M = 112, 193, 141$		

Original weight of rubber I + II: 0.7369 g. (the solution took place 8 days at 50°). Temperature of the supercooling bath: 41.1° .

	Temperature, Degrees	Time, Min.
Inoculation	0.670	0
Beginning of crystallization	0.651	4
Supercooling	0.620	27
Highest point	0.700	104
$\Delta = 0.458^\circ$ $M = 1110$		
Inoculation	0.690	0
Beginning of crystallization	0.672	4
Supercooling	0.589	25
Highest point	0.721	99
$\Delta = 0.437^\circ$ $M = 1160$		
Inoculation	0.700	0
Beginning of crystallization	0.695	4
Supercooling	0.644	30
Highest point	0.702	94
$\Delta = 0.456^\circ$ $M = 1110$		
$M = 1110, 1160, 1110$		

As can be seen, entirely different values are obtained for the same rubber according to the concentration and duration of the heating. In all cases, as with cholesterol and cyclo-rubber, the rate of crystallization is very much retarded compared to that of pure menthol. The process lasts much longer, so that the supercooling bath has a much greater influence. In addition, a large part of the heat of crystallization of the rubber solution is lost because the interval of time between the beginning of crystallization and the supercooling point is much greater than with pure menthol.

II. The Determination of the Molecular Weights of Polymeric Substances in Camphor. (M. Asano, H. F. Bondy, and R. Signer)

Execution of the Molecular Weight Determinations.—One hundred mg. of camphor and 5–20 mg. of the substance were heated at 180° in a sealed tube for about 5 min. Low molecular substances, like paraffin, etc., can be poured in in powdered form, while high polymeric substances must be deposited as a film in the tubes.

For the molecular weight determinations a middle fraction distilled from natural camphor was used. About 5 small melting point tubes were filled from the tube of the melted down mass; these were closed by melting and the melting point in a paraffin bath read off to 0.10° by a thermometer. Between the beginning of the fusion and the disappearance of the last crystal, which was the point that could be read in the most precise way, and which was regarded as the true melting point, there was an interval of about 0.3° . The melting point depended greatly upon

the rate of increase in temperature. In all the determinations this was maintained constant at 1–1.5° per min. In this way the individually determined melting points varied, at the most, 0.6°. The average was taken for the five determinations which came within 0.2° of the correct melting point.

Example: 0.1383 g. camphor; 0.00110 g. cyclo-rubber. Melting point: 176.4° 176.2°, 176.5°, 176.2°, 176.3°, 176.2°, 176.3°, 176.3°.

Results of the Determinations

A. Simple Paraffin Hydrocarbons.

	Camphor in G.	Substance in G.	Content in % Approx.	$\Delta_1 - \Delta_2$	Molecular Estd.	Weight Found
Dicetyl ^{39a}	0.2001	0.0156	8	6.6	450	472
Pentatriacontane	0.1193	0.0065	5	4.4	492	490
Hexacontane ⁴⁰	0.1954	0.0248	10	6.4	842	790

B. *Paraffin Mixtures*.—From a hard paraffin there were obtained by fractional distillation in a high vacuum 5 substances, whose melting points and ebullioscopic molecular weights in benzene were determined.⁴¹ The molecular weight in camphor of two of these fractions was studied.

Paraffin, Melting Point	Camphor in G.	Substance in G.	Content in %	$\Delta_1 - \Delta_2$	Molecular Weight In Camphor	Molecular Weight In Benzene
48–51°	0.1838	0.0152	12	10.1	330	335
75–78°	0.1638	0.0250	15	8.2	740	742

It appears from these experiments that the Rast method of molecular weight determination gives correct values with saturated paraffin hydrocarbons.

C. *Rubber and Gutta-percha*.—The molecular weights of pure rubber and pure gutta-percha, dried in high vacuum to constant weight, were determined.

	Camphor in G.	Substance in G.	Content in %	$\Delta_1 - \Delta_2$	Molecular Weight in Camphor
Rubber	0.1808	0.0099	5	1.0	2200
	0.1414	0.0141	10	1.8	2200
Gutta-percha	0.1261	0.0058	5	2.0	900
	0.2063	0.0183	10	3.1	1100
	0.1409	0.0141	10	3.9	1050
	0.1475	0.0158	10	3.7	1150
	0.2930	0.0292	10	3.0	1350
	0.1341	0.0261	20	7.0	1100

Here we are able to confirm the observations of Pummerer. Long heating with camphor resulted in essentially the same values. This indicates that a gradual cracking of the molecule does not occur.

	Camphor in G.	Substance in G.	Content in %	Time of Fusion	$\Delta_1 - \Delta_2$	Molecular Weight in Camphor
Gutta-percha	0.2930	0.0292	10	10 min.	3.0	1300
				1 hr.	3.2	1250
				5 hrs.	4.4	900
				10 hrs.	4.0	1000
Rubber	0.1414	0.0141	10	10 min.	1.8	2200
	0.0984	0.0112	11	1 hr.	2.8	1620
	0.1190	0.0141	12	5 hrs.	3.9	1200
	0.1626	0.0179	11	20 hrs.	2.1	2100
	0.1335	0.0138	10	20 hrs.	2.4	1700

The molecular weights, which are too small, depend on impurities of low molecular weight, which even in very slight concentration depress the melting point about 1–2°. If rubber or gutta-percha is slightly oxidized by standing in air it

yields at 150° in high vacuum a considerable quantity of volatile components as shown in the following experiments.

APPROXIMATE PERCENTAGE DECREASE IN WEIGHT OF THE TOTAL QUANTITY
ON 10 DAYS' VACUUM OF 0.1 MM.

	Oxygen Content, %	At 40°	At 150°
Pure rubber	0	0.0	0.2
Oxidized rubber	About 1	0.0	5.0
Oxidized balata	About 5	0.0	20.0

Substances of low molecular weight might also have formed by the catalytic decomposition of camphor.

Identification of Low Molecular Substances.—Substances of low molecular weight formed during the camphor determination of rubber and gutta-percha which seem to have too small a molecular weight, could be identified the following way: Camphor and a high molecular substance were placed in the side piece of a T-tube with two sealed ends; the tube was highly evacuated and sealed. Immersion in a paraffin bath at 180° dissolved the substance in the camphor. The empty side was cooled to -80°, that containing the fused material was warmed to 100°, whereupon the camphor sublimed off in a few minutes. The melting point of camphor was determined in this side. It was 1-1.5° lower than that of non-sublimed camphor and of sublimed camphor containing no high molecular substance.

	Camphor in G.	Substance in G.	Substance in %	Melting Point		Depression
				Camphor	Sublimed Camphor	
Gutta-percha	0.0820	0.0080	10	179.9	179.2	0.7
	0.0755	0.0083	11	179.9	178.8	1.1
	0.0510	0.0064	12	179.9	178.6	1.3
	0.0523	0.0065	12	179.9	179.2	0.7
Rubber	0.0582	0.0062	11	179.9	179.0	0.9
	0.1032	0.0114	11	179.9	178.5	1.4
	0.0700	0.0084	12	179.9	178.8	1.1
	0.0985	0.0104	10	179.9	179.0	0.9

D. Decomposition Products of Gutta-percha and of Rubber.—The molecular weight was cryoscopically determined in benzene for various cyclo-rubbers and cyclo-gutta-perchas.⁴² The following molecular weights were obtained in camphor.

	Camphor in G.	Substance in G.	Content in %	$\Delta t - \Delta t_0$	Molecular Weight in Camphor	Molecular Weight in Benzene
Cyclo-gutta-percha from xylene (unfractionated)	0.2092	0.0094	5	1.5	1200	3500
	0.2009	0.0250	12	3.2	1550	3500
	0.1071	0.0273	25	6.0	1700	3500
Cyclo-rubber from xylene (unfractionated)	0.1321	0.0051	4	0.9	1700	8500
	0.1683	0.0125	7	1.3	2200	8500
	0.1769	0.0146	8	1.7	1950	8500
Cyclo-rubber from xylene (insoluble in ether)	0.1723	0.0099	6	1.0	2250	12000
	0.1383	0.0110	8	1.6	2000	12000
	0.1282	0.0107	8	1.4	2400	12000
	0.1728	0.0150	9	1.4	2400	12000
Cyclo-rubber from ben- zene (insoluble in ether)	0.2518	0.0140	6	0.9	2500	Infinity
	0.1955	0.0203	10	1.7	2450	Infinity

These products, like rubber and gutta-percha, gave too small molecular weights in camphor. Here, too, the substances of low molecular weight, through sublimation of the camphor, were proved to be the cause of the great depression in the melting point.

	Camphor in G.	Substance in G.	Mixture in %	Melting Point Camphor	Point Sublimed Camphor	Depression
Cyclo-rubber						
Molecular weight,	0.0628	0.0072	12	179.9	178.8	1.1
12000	0.0687	0.0083	12	179.9	178.9	1.0

Two cyclo-rubbers were fused to complete solution, using 2 g. of cyclo-rubber to 20 g. of camphor. The camphor was subsequently removed with methyl alcohol. The products were purified by precipitation from benzene with methyl alcohol and then the molecular weight in benzene and camphor was determined again.

CYCLO-RUBBERS BEFORE AND AFTER FUSION IN CAMPHOR

			Before	After
Cyclo-rubber (insoluble in ether)	Composition	% C	88.01	87.96
		% H	11.94	12.00
	Molecular weight in benzene		12500	12000
	Molecular weight in camphor		2400	2500
	Viscosity in benzene (time of discharge in sec.)	1-molar	122	120
		1/2-molar	72	71
		1/4-molar	56	55
Cyclo-rubber (soluble in ether)	Composition	% C	87.98	87.93
		% H	12.05	12.92
	Molecular weight in benzene		4800	4100
	Molecular weight in camphor		1400	1400
	Viscosity in benzene (time of discharge in sec.)	1-molar	73	74
		1/2-molar	55	55
		1/4-molar	49	49

The average molecular weight of the two different cyclo-rubbers did not change after solution in fused camphor and reprecipitation from the benzene solution. Strange to say, the values in camphor were the lower. However we assume that in this case traces of autooxidized cyclo-rubber, on solution in melted camphor, were decomposed to lower molecular components. These decomposition products remained in solution on reprecipitation, and were therefore not recognizable in the molecular weight determinations in benzene. Weakly autooxidized cyclo-rubber could be dried at 40–50° to constant weight. On heating to 150° *in vacuo*, however, it lost weight, in fact 5–8 per cent.

Finally, molecular weight determinations of gutta-percha and cyclo-rubbers were carried out in such a way that the melting point tubes were filled with CO₂ and nitrogen, respectively, in order to avoid autooxidation. However a slight quantity of air in the melting point tubes had no appreciable effect.

References

- ¹ Cf. *Kautschuk*, 1927, 63, for 12th communication.
- ² *Kautschuk*, 1927, 233.
- ³ *Ber.*, 60, 2167 (1927).
- ⁴ *Ibid.*, 59, 2973 (1926).
- ⁵ *Ann.*, 438, 294 (1924).
- ⁶ *Ibid.*, 438, 303 (1924).
- ⁷ *Ber.*, 60, 2167 (1927).
- ⁸ *Ibid.*, 61, 1591 (1928).
- ⁹ *Kolloidchem. Beihefte*, 22, 63 (1926).
- ¹⁰ Cf. Bary and Hauser, *Kautschuk*, 1928, 97, who with x-ray measurements confirm this discovery.
- ¹¹ *Naturwissenschaften*, 14, 320 (1926).

- ¹² Staudinger, *Ber.*, **59**, 3019 (1926).
- ¹³ *Helvetica chim. acta*, **8**, 307 (1925).
- ¹⁴ Staudinger and Bruson, *Ann.*, **447**, 97 (1926).
- ¹⁵ Weber, *Ber.*, **33**, 784 (1900).
- ¹⁶ Kautschuk, **1927**, 64.
- ¹⁷ *Ibid.*, **1927**, 64; Meyer, *Z. angew. Chem.*, **1928**, 943.
- ¹⁸ *Ber.*, **60**, 2167 (1927).
- ¹⁹ Kautschuk, **1925**, No. 1 and 2; **1927**, 64, 237; *Z. angew. Chem.*, **1925**, 226.
- ²⁰ Staudinger and Fritsch, *Helvetica chim. acta*, **5**, 785 (1922); Staudinger, *Ber.*, **57**, 1203 (1924).
- ²¹ Staudinger and Widmer, *Helvetica chim. acta*, **7**, 842 (1924).
- ²² Dissertations of Wehrli and Brunner, Zürich, **1926**; *Ber.*, **59**, 3032 (1927).
- ²³ Staudinger, Johner, Signer, Mie, and Hengstenberg, *Z. phys. Chem.*, **126**, 425 (1927).
- ²⁴ *Ber.*, **59**, 3027 (1926). Such a lattice was termed a high polymeric lattice.
- ²⁵ A crystal, such as that in Fig. 4 in the *Annalen* article of Pummerer, can originate only from molecules of the same length.
- ²⁶ Staudinger and Fritsch, *Helvetica chim. acta*, **5**, 785 (1922); *Ber.*, **57**, 1203 (1924).
- ²⁷ *Gazz. chim. ital.*, **29**, ii, 258 (1899).
- ²⁸ Staudinger and Widmer, *Helvetica chim. acta*, **9**, 529 (1926); Bondy, *Dissertation*, Freiburg i. Br., **1928**.
- ²⁹ Pummerer, *Ber.*, **61**, 1595 (1928).
- ^{29a} Molecular weight determinations in benzylidene-camphor were not carried out before, since the depressions of concentrated solutions are very small.
- ³⁰ Staudinger, *Ber.*, **59**, 3030 (1926).
- ³¹ *Ber.*, **61**, 1945 (1928).
- ³² Staudinger, *Kautschuk*, **1927**, 237.
- ³³ Staudinger, Johner, Signer, Mie, and Hengstenberg, *Z. phys. Chem.*, **126**, 435 (1927).
- ³⁴ *Kautschuk*, **1927**, 237.
- ³⁵ *Z. angew. Chem.*, **41**, 942 (1928); Meyer and Mark, *Ber.*, **61**, 2427 (1928).
- ³⁶ Pummerer and Nielsen, *Ber.*, **60**, 2170 (1927).
- ³⁷ The menthol was manufactured by Schimmel & Co. and was distilled before use.
- ^{37a} Supercooling means the lowest reading of the thermometer.
- ³⁸ Bondy, *Dissertation*, Freiburg, **1928**. This cyclo-rubber sintered at about 115° and melted at 143°. It analyzed 80.07% C, 11.56% H (calculated 88.15 and 11.85%, respectively).
- ³⁹ The rubber was purified according to the directions of Pummerer and Pahl, *Ber.*, **60**, 2152 (1927). It analyzed 88.21% C, 12.00% H (calculated 88.15% and 11.85%, respectively).
- ^{39a} This preparation was obtained from A. Grün, Grenzach.
- ⁴⁰ A sample of this preparation was obtained from the I.-G. Farbenindustrie of Ludwigshafen.
- ⁴¹ Unpublished work of R. Nodzu.
- ⁴² Staudinger and Widmer, *Helvetica chim. acta*, **9**, 529 (1926).

Isoprene and Rubber

VII. The Fractionation of Balata¹

H. Staudinger and H. F. Bondy

On the basis of earlier experiments with synthetic materials, compounds of high molecular weight are not composed of a single substance, but consist of a mixture of homologous polymers.² The individual members of a polymeric homologous series differ very little in physical and chemical properties, and therefore a mixture of polymeric homologous products such as is obtained in the polymerization of the monomer cannot as a rule be decomposed into simple compounds by means of solvents, but merely into mixtures of products of low and high molecular weight. Such separations have been carried out, for example, in the case of polyvinylacetates,³ polystyrols,⁴ polyindenes,⁵ polyanetholes,⁶ and polyethyleneoxides.⁷

On the basis of these experiments it was assumed that natural products of high molecular weight likewise consist of a mixture of polymeric homologs. Thus purified rubber, for example, according to our views is not such a completely homogeneous hydrocarbon that all the molecules have the same length, but consists of a mixture of perhaps 100 or more polymeric homologs.⁸ Pummerer's⁹ decomposition of rubber into sol- and gel-rubber, according to our experiments, is due to the fact that rubber consists of easily soluble polyprenes and difficultly soluble polyprenes, all belonging to the same polymeric homologous series.

Of course there is the possibility that, in forming compounds of high molecular weight, nature produced primary molecules of uniform size, and that the mixture of polymeric homologs was formed only later through decomposition. In that case the natural products would differ in constitution from the synthetic material. They would not be polymerically uniform but completely uniform compounds in the sense of classical organic chemistry. The fact that in life processes methods are possible which we cannot realize in the laboratory is well known.

Such a finding would not, of course, contradict our former view that natural products, such as rubber and balata, are of high molecular weight in the sense of classical structural chemistry. Our former work¹⁰ has indicated a similar structure for rubber and gutta-percha. Here it is simply a question whether or not the macromolecules of these natural products have a uniform length.

In order to reach a decision, we first of all investigated balata, since it is prepared pure more easily than rubber. It was made from balata latex which was supplied to us through the courtesy of the management of the Norddeutsche Seekabelwerke, Nordenham.¹¹ The balata thus obtained is a flocculent, cellulose-like mass, which looks like gutta-percha and crystallizes like it.

Separation of the Balata into Polymeric Homologous Fractions

The separation of the balata into individual fractions was easily accomplished, since it crystallizes out on cooling solutions in warm benzene, toluene, or xylene.¹² By proper cooling to various temperatures, the balata does not precipitate out all at once but in separate fractions. On cooling to -10°C . the balata finally precipitates completely.

We assume that, in this fractional crystallization, products of high molecular weight, which are difficultly soluble, are the first to separate out, and that products of lower molecular weight, which are more easily soluble, remain behind in the

mother liquor; for, in working with polymeric, homologous substances, it is our common experience¹³ that those portions of higher molecular weight are more difficultly soluble than those of lower molecular weight. Accordingly there is the same interdependence between the solubility of highly polymerized substances and the molecular weight as in the case of ordinary organic compounds.¹⁴ This is to be expected, for the solubility decreases with increasing molecular size, and, therefore, with the increase of the intermolecular forces.

In order to show that substances differing in average molecular weight are really present in the individual fractions, the fluidity of solutions of equal concentration was determined by means of a Ubbelohde viscosimeter. In the case of semi-colloids it was shown that the differences in viscosity, that is, in the fluidity of solutions of equal concentration, were due to differences in molecular size and not to different degrees of association or micellar size.¹⁵ In a similar way it could be shown that the homopolar hydrocarbon, balata, is molecularly dispersed in dilute solution and does not form micelles. (Cf. 18th Communication.)

Table I shows that the most difficultly soluble fraction yields the solution with the highest viscosity, and that the viscosity of the solution decreases with increased solubility of the fraction. Hence we conclude that balata consists of a mixture of polymeric homologs, which differ from each other in the length of the molecules.

This reasoning, of course, holds true only if the balata fractions are polymerically uniform. It is much more difficult to prove this than in the case of simple synthetic polymeric substances such as the polystyrols.¹⁶ For example, there is the possibility that the portions that are more easily soluble, giving solutions of lower viscosity, are constituted differently from the more difficultly soluble portions, which give solutions of higher viscosity, and that the differences in physical properties are due, not to differences in the size of the molecule, but to a difference in structure. Thus balata might consist of more or less cyclicized products,¹⁷ which show the differences mentioned. Therefore, we determined with iodine chloride the double bonds in the balata before fractionation, and then in the first and last fractions, and we found that there is a double bond to a base molecule present in all fractions.¹⁸ Accordingly, the balata fractions are polymerically uniform.

TABLE I

Substance	Quantity in 17 g. Balata	Relative Viscosity of a 0.5 Molar Solution in Benzene at pressure of			Per cent Decrease of η_r on Increasing the Pressure from 10 to 60 cm. Hg
		10 cm.	30 cm.	60 cm.	
Original balata	17 g.	40.39	36.56	34.65	13.9
Fraction I	6 g.	53.12	49.02	46.58	12.3
Fraction II	5 g.	40.18	38.38	36.63	8.9
Fraction III	2 g.	34.42	32.99	32.14	6.8
Fraction IV	0.8 g.	31.85	30.26	29.72	6.5
Fraction V	3 g.	26.99	26.85*	25.16	6.1

Constitution of the Original Balata

The foregoing experiments show that the balata examined consists of a mixture of products of high and low molecular weight. Now there is the question, is this mixture already present in the original balata or is it formed subsequently, due to the fact that part of the long similar molecules are decomposed by the action of oxygen? Leupold¹⁹ showed that the oxygen content of solvents affects balata, breaking down its structure. In order to exclude the possibility of such action by oxygen, we worked in an atmosphere of carbon dioxide, and undertook all the fractionations in the absence of air.

Of course, considering the sensitivity of balata, there is always the possibility

that the balata latex used is already changed by autooxidation; moreover, it is not conclusively shown by these experiments that natural balata, like highly polymerized synthetic materials, consists of a mixture of polymeric homologs, and there is always the possibility that the natural product consists of wholly similar molecules of a definite order of magnitude. This question will be decided only when the balata is examined at its source, in other words, when the balata latex is tapped off in the complete absence of oxygen, and the hydrocarbon isolated from it in the absence of air.

Deviations from the Law of Hagen-Poiseuille

It has been shown in the case of the polystyrols that the deviations from the Hagen-Poiseuille law are more pronounced in the case of high molecular substance than in the case of the substances of lower molecular weight. In the case of semi-colloidal substances, they do not occur, or only to a slight extent.²⁰ A similar observation is made in the case of balata. If one compares the deviations from the Hagen-Poiseuille law shown by the various fractions (cf. Table I, Column 3), it appears that they are different in solutions of the same concentration, and, moreover, they are greatest in the solution having the greatest viscosity, and therefore the solution containing the largest molecules. Hence the deviations here also are due not to any special structural feature of the solution but to the presence of large molecules.²¹

Experimental Part

Raw Material.—The balata latex obtained through the negotiations of the Norddeutsche Seekabelwerke A.-G., Nordenham, closely resembles rubber latex in appearance, and hence is a white milky liquid containing about 40% of hydrocarbon. Pure balata was isolated from this latex in the following way: The latex was diluted with ten times as much water, and the resulting 4% solution was run into three times as much methyl alcohol, whereupon the balata separated out in yellowish threads. For further purification the precipitate was dissolved in carbon tetrachloride, separated from impurities by centrifuging, and filtered through a Soxhlet filter. Thus the procedure was just the same as that followed in the purification of gutta-percha.²² The colorless carbon tetrachloride solution was stirred into three times as much methyl alcohol, whereupon the balata separated out as a white fibrous mass, which was wholly pure after a subsequent precipitation.

Sample	CO ₂	H ₂ O
3.384 mg.	10.92 mg.	3.62 mg.
3.333 mg.	10.79 mg.	3.57 mg.

Calculated for (C₈H₈)_x: carbon, 88.15; hydrogen, 11.85. Found: carbon 88.01, 88.29; hydrogen 11.97, 11.98.

The solubility of balata is very similar to that of rubber. Hence it dissolves very easily in carbon disulfide and carbon tetrachloride and in benzene, toluene, and xylene on warming slightly; however, from the latter solutions it separates out as a flocculent mass on cooling to -15° C., while from the former solutions no such separation occurs due to the greater solubility. Balata dissolves with difficulty in cyclohexane; only small portions dissolve in ether, and it is yet to be found whether treatment with ether will effect a separation into high and low molecular portions as in the case of rubber. Balata is insoluble in alcohol, acetone, and petroleum ether.

Preparation of the Balata Fractions

Seventeen grams of balata were dissolved in 500 cc. of xylene at about 25° C. The highly viscous 0.5 molar solution thus obtained was cooled to 10° C. in a filter cylinder, stirring constantly. After a short time the solution became opaque, and part of the balata separated out. After standing for 24 hours, the precipitated latex was centrifuged, it being necessary to proceed in such a way that the precipitate does not dissolve either wholly or partly, due to warming. After being centrifuged for one-half hour, the clear solution is poured off, the crystallized portion redissolved in xylene at 25° C., cooled again with constant stirring until the first sign of opacity, and let stand at this temperature for three hours. The dissolved portion is added to the first solution, while the residue is treated in the same way a third time. The most insoluble portion is then dissolved once more in xylene for a further purification, and the balata is precipitated by adding the solution drop by drop to a mixture of methyl alcohol and acetone. In this way the most difficultly soluble portion, Fraction I, is isolated. A second fraction is separated from the combined solutions by further cooling to lower temperature, and is obtained in the same way by dissolving and purifying three times. Fraction II is thus prepared. In exactly the same way Fractions III and IV are obtained from the mother liquor, and finally the most soluble fraction V separates out on cooling the xylene solution severely. After this only traces remain in the xylene; hence, by cooling to -12° C. the balata can be almost completely precipitated.

These five fractions were obtained in the quantities listed below, and at the temperatures indicated.

Fraction I	6 g.	At about	10° C.
Fraction II	5 g.	At about	5° C.
Fraction III	2 g.	At about	3° C.
Fraction IV	0.8 g.	At	0° C.
Fraction V	3 g.	At about	-12° C.

Each fraction was dried to constant weight in high vacuum.

Determination of Double Bonds

In order to see if the various balata fractions were polymerically uniform, the double bonds were titrated with iodine chloride, as was done in the previous work.²³

Fraction I: 0.1023 g. substance consumed 0.3821, 0.4184 g. I. As HI 0.113, 0.0071 g. I.

HI through substitution: 94.3, 96.4% double bonds.

HI through cyclicization: 100.2, 99.9% double bonds.

Fraction V: 0.1012, 0.1089 g. substance consumed 0.3807, 0.4103 g. I. As HI 0.0056, 0.0099 g. I.

HI through substitution: 97.9, 96.2% double bonds.

HI through cyclicization: 100.9, 101.0% double bonds.

Original balata: 0.1078, 0.1052 g. substance consumed 0.4216, 0.4019 g. I. As HI 0.0127, 0.0141 g. I.

HI through substitution: 98.6, 95.2% double bonds.

HI through cyclicization: 104.9, 102.4% double bonds.

Notes

¹ Sixteenth communication, *Ber.*, **62**, 2411 (1929).

² Staudinger, *Ibid.*, **59**, 3019 (1926).

³ Staudinger, Frey, and Starck, *Ibid.*, **60**, 1782 (1927).

⁴ Staudinger, Brunner, Frey, Garbsch, Bruson, Signer, and Wehrli, *Ibid.*, **62**, 241 (1929).

⁵ Staudinger, Ashdown, Brunner, Bruson, and Wehrli, *Helv. Chim. Acta*, **12**, 934 (1929).

⁶ Staudinger, Brunner, *Ibid.*, **12**, 972 (1929).

⁷ Staudinger, Schweitzer, *Ber.*, **62**, 2395 (1929).

⁸ Cf. Staudinger, *Kautschuk*, **1927**, 64.

⁹ Cf. Pummerer, *Ibid.*, **1927**, 233; also Pummerer, Andriessen, and Gündel, *Ber.*, **61**, 1583 (1928).

¹⁰ Cf. Staudinger and Fritsch, *Helv. Chim. Acta*, **5**, 785 (1922); also the résumé, *Kautschuk*, Aug.-Sept., **1925**; *Kautschuk*, **1927**, 63, Nos. 5 and 6, 1929. Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

¹¹ This opportunity may be taken to thank the management of this form.

¹² Similar observations were made by Kirchhof in a paper read to the Rubber Society in June, 1929; cf. *Kautschuk*, **1929**, 175. In the discussion that followed H. F. Bondy remarked that he had made similar observations some time before.

¹³ Compare the separation of mixtures of polystyrols, polyindenes, polyanetholes, polyvinylacetates, and polyethyleneoxides into easily soluble and difficultly soluble fractions, which are of lower and higher molecular weight, respectively. Cf. Notes 3 to 7.

¹⁴ Cf. the contrary views of Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929).

¹⁵ Cf. Staudinger, *Ber.*, **59**, 3019 (1926) and Staudinger and Heuer, *Ibid.*, **63**, 222 (1930); Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

¹⁶ Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929), apply to raw rubber and cellulose derivatives theories on polymeric homologous series developed in the study of synthetic polymers, and from differences in viscosity likewise infer differences in the size of the molecules. This view is tenable only when it is shown that these products are polymerically uniform.

¹⁷ Staudinger and Widmer, *Helv. Chim. Acta*, **9**, 529 (1926).

¹⁸ In these titrations hydrogen halide splits off to some extent. If it is assumed that this is the result of substitution, then only 95% of the double bonds are present; in the case of the more probable assumption that it is produced by cyclicization, as mentioned above, there is a double bond to each base molecule.

¹⁹ Cf. 18th communication.

²⁰ Staudinger and Machemer, *Ber.*, **62**, 2921 (1929); Staudinger and Heuer, *Ibid.*, **62**, 2933 (1929).

²¹ Staudinger and Frey, *Ibid.*, **62**, 2909 (1929); cf. Wo. Ostwald, *Kolloid-Z.*, **36**, 99 (1925).

²² Cf. Staudinger and Bondy, *Ann.*, **468**, 36 (1929).

²³ Cf. *Ind. Eng. Chem.*, **19**, 531 (1926); also *Ann.*, **468**, 36 (1929).

Isoprene and Rubber

XVIII. Viscosity Studies on Balata¹

H. Staudinger and E. O. Leupold

Varied views prevail as to the structure of the colloidal particles present in a rubber solution. According to Harries, Pummerer,² and many others, these colloidal particles are formed through the association or aggregation of smaller molecules. According to Meyer and Mark³ they have a micellar structure, the micelles forming through the apposition of main valence chains. On the other hand, it was assumed by one of the present authors that the elementary particles in a colloidal solution of rubber are identical with the rubber molecules, these large, especially labile molecules being called macromolecules.⁴ Thus the existence of much larger molecules than any hitherto known was postulated. This view was confirmed by the conversion of rubber to hydro-rubber capable of forming colloidal solutions,⁴ and also by the pyrogenic decomposition of rubber.⁵

In order to decide definitely between the two conceptions, the stability of the colloidal particle in a rubber solution was studied by means of viscosity measurements at various temperatures as was done in the case of the polystyrols.⁶ If these colloidal particles form aggregates or if they have a micellar structure, they should decrease in size with increase in temperature, and this change should be evidenced by a diminution of the specific viscosity of the colloidal solution. On the other hand, if such a solution is composed of molecules, the specific viscosity at various temperatures is the same, provided that the molecules are not decomposed at higher temperatures. This line of research led to an explanation of the constitution of the colloidal particles in a polystyrol solution⁶ and was now applied to balata, since the latter is especially easily purified.⁷

Autooxidation of Balata in Solution

The first viscosity measurements on balata solutions at various temperatures gave confusing results.⁸ The specific viscosity of a 0.2 molar solution in tetralin is less at 60° C. than at 20° C.; hence existent associations were changed by heating. Strange to say, on cooling the solution did not have its original viscosity, but a lesser one. It was believed that such an irreversible diminution in viscosity was due to a diminution in the size of the molecule, and it was shown that the latter was caused by small quantities of oxygen contained in the solvent.⁹ If the corresponding viscosity determinations were made in an atmosphere of pure nitrogen, using solvents free from air, these anomalies vanished.

Balata—and this is true also of rubber—is so sensitive that when it is dissolved in a solvent containing air the molecules are partly decomposed due to oxidation, and this change is evidenced by a fall in viscosity. (Cf. Table I, Series I.) Therefore, all viscosity determinations on solutions of rubber, gutta-percha, and balata which are not carried out in the complete absence of air, and using solvents free from air, are useless for accurate results.

TABLE I

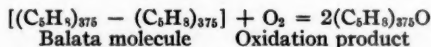
SPECIFIC VISCOSITY OF A 0.2 MOLAR SOLUTION OF BALATA IN TETRALIN

Series No.	Tetralin (Air-free)			Tetralin (Containing Air)			Tetralin (Containing Oxygen)		
	Heated to 20° C.	60° C.	Cooled to 20° C.	Heated to 20° C.	60° C.	Cooled to 20° C.	Heated to 20° C.	60° C.	Cooled to 20° C.
I. Immediately after solution	5.74	5.15	5.74	5.06	4.52	4.91	4.36	3.79	4.06
II. After heating 20 hrs.	5.60	4.98	5.59	2.81	2.54	2.67	0.92	0.83	0.89
III. After heating 100 hrs.	5.45	4.91	5.45	2.65	2.41	2.57	1.31	1.19	1.27
IV. After heating 400 hrs.	5.38	4.74	5.37	2.44	2.22	2.36	1.01	0.91	0.97
V. After standing 400 hrs. at 20° C.	5.74	5.13	5.74	3.43	3.05	3.30	1.58	1.40	1.50

In order to show the effect of air or oxygen more clearly, the balata solutions were heated to 60° C. in the presence of small quantities of air or oxygen and also in an atmosphere of pure nitrogen. (See Series II, III, and IV of Table I.) In this way confirmation was afforded of the view that air or oxygen has a strong breaking-down action. On the other hand the balata was hardly changed at all on prolonged heating at 60° C. in the absence of air. Accordingly its molecules are quite stable, as has been pointed out before.¹⁰

Hence these experiments show that balata molecules are very sensitive to oxygen. In the case of the polystyrols it has been found that large molecules or macromolecules are much more sensitive to reagents or increase in temperature than semi-colloidal molecules of similar structure.¹¹ The lability of the balata molecule as compared to the polystyrol molecule is much increased by the presence of the double bond. Therefore, balata is much more sensitive to oxygen than the macromolecules of polystyrols, which as shown by viscosity measurements are not oxidized in solvents containing oxygen.

How small a quantity of oxygen is necessary to produce a marked decomposition of the balata molecule is shown by the following calculation: Balata having an average molecular weight of 51,000¹² and therefore containing 750 elementary molecules to the macromolecule is split by one molecule of oxygen; in dilute solution the specific viscosity is thereby cut in half. Therefore, 3750 l. of 0.2 molar tetralin solution are similarly changed by the action of 22.4 l. of oxygen, or 1 cc. is affected by the presence of 0.006 cc. of oxygen or 0.03 cc. of air enough to split the molecule and cut the viscosity in half. This small quantity of oxygen cannot be demonstrated in the reaction product. If the reaction is formulated according to the following equation:



then the oxidation product contains only 0.06% of oxygen, a quantity too small to be shown by analytical means. However, the above reaction can be followed very easily through the changes in viscosity. Therefore, viscosity determinations will play a very important role in the chemistry of high molecular substances, since it has been hereby shown that real molecules are present in dilute solution and the viscosity of such a solution depends on the molecular weight of the dissolved substance;¹³ for these determinations afford the simplest means of showing the changes in the macromolecules.¹⁴

Balata Solutions Contain Macromolecules

After it was found that the disturbing effects in the viscosity determinations could be attributed to the oxygen contained in the solvent, it was possible by carefully excluding it to show whether molecules of balata or micelles were present in dilute solution. The former is the case, for in a 0.025 molar solution the specific viscosity does not change on heating to 60° C., and in a 0.05 and 0.1 molar solution but very little, an indication that in such dilute solutions (less than 0.5%) micelles or aggregations sensitive to temperature changes are not present. (Cf. Table II.)

Moreover, it has also been shown that balata molecules are not strongly solvated, as has recently been assumed by Fikentscher and Mark¹⁵ in the case of rubber; for the size of such a solvate film would necessarily vary with increasing temperature, and this would be evidenced by a marked decrease in viscosity.

TABLE II
SPECIFIC VISCOSITY OF TETRALIN SOLUTIONS OF BALATA IN AN ATMOSPHERE OF NITROGEN

Molarity	At 20° C.	At 40° C.	At 60° C.	Cooled again to 20° C.	Deviation of η_{sp}/c 60 from η_{sp}/c 20 in %
0.025	0.33	0.33	0.33	0.33	0
0.05	0.75	0.73	0.71	0.75	5
0.1	1.78	1.74	1.61	1.76	9
0.2	5.75	..	5.16	5.74	10
0.3	10.09	9.5	8.83	10.07	12

At this point it may be pointed out that it is not merely a question of nomenclature whether the particles in a colloidal solution of rubber or balata are called macromolecules or are called micelles,¹⁶ but for the understanding of such substances according to the theories of organic chemistry it is of fundamental importance whether they are composed of such large molecules, the changes in the substance being due to internal rearrangements, or whether they have a micellar structure, the changes being due to variations in particle size, as has thus far been accepted by organic chemistry. The present work answers the question by definitely proving the existence of the macromolecule.

Notes

¹ See 17th communication above.

² Pummerer, Nielson, and Gündel, *Ber.*, **60**, 2161 (1927); Pummerer and Gündel, *Ibid.*, **61**, 1591 (1928).

³ Meyer and Mark, *Ibid.*, **61**, 1945 (1928).

⁴ Staudinger and Fritsch, *Helv. Chim. Acta*, **5**, 785 (1922); Staudinger, *Kautschuk, Aug. and Sept.*, 1925.

⁵ Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

⁶ Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).

⁷ Similar results are obtained with rubber, and will be reported later.

⁸ The measurements were made with an Ubbelohde viscosimeter at various pressures, though in the present article only the results obtained at 30 cm. of mercury are given. The dependence of the viscosity on the pressure is not very great in the case of balata; this matter will be treated in a special work.

⁹ Organic solvents sometimes dissolve considerable oxygen.

¹⁰ Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

¹¹ Staudinger, Frey, Garbsch, and Wehrli, *Ber.*, **62**, 2913 (1929).

¹² For the molecular weight of balata, see the following article.

¹³ Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

¹⁴ Corollaries of importance to biology will be treated elsewhere.

¹⁵ Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929).

¹⁶ Cf. the models of Ostwald, *Ibid.*, **49**, 60 (1929).

Isoprene and Rubber

XIX. The Molecular Size of Rubber and Balata¹

H. Staudinger and H. F. Bondy

It was shown in the preceding work that a very dilute solution of balata in an organic solvent contains macromolecules in solution and not micelles. The same is true of rubber. On the basis of these findings it is possible to calculate the molecular weight of rubber and balata from viscosity measurements by means of the formula developed in a previous work:² $M = \eta_{sp}/c \cdot K_m$. The supposition is made that the molecules of rubber and balata have the form of threads and double threads, respectively.³ Also it is necessary to determine the constant K_m , and this may be calculated in the case of low molecular products, where the average molecular weight can be determined as well as the viscosity of the solutions. Such semi-colloidal decomposition products were obtained by heating rubber or gutta-percha in either tetralin or xylene.⁴ As shown by the following table the four samples thus obtained gave the constant: 0.3×10^{-3} .⁵

TABLE I
Relative Viscosity
 $\eta_r = \eta_c/\eta_L$
of a 0.025
Molar Solution
in Benzene

Substance	Molecular Weight in Benzene	Relative Viscosity of a 0.025 Molar Solution in Benzene	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/c	$K_m = \frac{\eta_{sp}}{cM} 10^3$
Rubber, broken down in tetralin	3400	1.263	0.263	1.052	0.31
Rubber, broken down in xylene	4250	1.285	0.285	1.140	0.27
Gutta-percha, broken down in tetralin	6400	1.507	0.507	2.028	0.32
Gutta-percha, broken down in xylene	2700	1.200	0.200	0.800	0.30

It is to be noted that the constants for rubber and gutta-percha are the same, although these hydrocarbons are believed to be stereoisomeric, rubber possessing the *trans*-form, gutta-percha the *cis*-form.⁶ Balata is essentially identical with gutta-percha. In the case of the stereoisomer, dichloroethylene, the *trans*-form is more viscous than the *cis*-form.⁷

In order to calculate the molecular weight of rubber and balata, the viscosities of their solutions were determined at such low concentrations that solutions of eu colloids would be approximately equivalent to those of semi-colloids. From the values thus obtained for the specific viscosity, the specific viscosity of a molar solution was calculated, assuming that the viscosity increased with the concentration. That this is actually the case is shown by the following experiments, where the value of η_{sp}/c was determined for various concentrations. The table shows that at lower concentrations this value is approximately constant, but in a 0.1 molar solution deviations occur.

TABLE II

THE EASILY SOLUBLE FRACTION OF RUBBER

Molarity c	Viscosity in Seconds According to Ostwald's Viscosimeter (Benzene = 41.4)	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/c	Deviation from η_{sp}/c in %
0.01	47.88	0.157	15.7	..
0.025	57.5	0.389	15.5	1
0.05	79.1	0.911	18.2	16
0.1	142.0	2.430	24.3	55

TABLE III

THE DIFFICULTY SOLUBLE FRACTION OF RUBBER

Molarity c	Viscosity in Seconds According to Ostwald's Viscosimeter (Benzene = 41.4)	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/c	Deviation from η_{sp}/c in %
0.01	50.5	0.220	22.0	..
0.025	63.9	0.543	21.8	1
0.05	101.1	1.442	28.9	31
0.1	189.0	3.565	35.7	62

TABLE IV

ORIGINAL BALATA

Molarity c	Viscosity in Seconds According to Ostwald's Viscosimeter (Benzene = 41.4)	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/c	Deviation from η_{sp}/c in %
0.01	48.0	0.159	15.9	..
0.025	57.4	0.386	15.4	3
0.05	73.4	0.773	15.5	2
0.1	118.8	1.870	18.7	17
0.25	355.0	7.575	30.3	90

From these specific viscosities determined at low concentrations, Table V shows a calculated molecular weight of 51,000 for the original balata before fractionation, for an ether-soluble fraction of rubber purified by Pummerer's method a molecular weight of 52,000, and for a difficultly soluble fraction, 73,000.

TABLE V

CALCULATED MOLECULAR WEIGHTS

Substance	Viscosity, Measured in Molarity	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/c	$M = \frac{\eta_{sp}}{c \cdot K_m}$ $K_m = 0.3 \times 10^{-3}$
Balata	0.025	0.386	15.4	51000
Rubber, easily soluble fraction	0.025	0.389	15.5	52000
Rubber, difficultly soluble fraction	0.025	0.543	21.8	73000

A similar value for rubber and gutta-percha has been obtained by Caspari⁸ from osmotic measurements. From a different point of view as to the structure of the colloidal particle, these values have been given for the weight of the micelle by Pummerer,⁹ Kröpelin,¹⁰ and Meyer and Mark.¹¹ Recently Ostwald¹² has shown that the lowest value for the weight of the micelle corresponding to Caspari's views can be designated as equivalent to the molecular weight.

These viscosimetric measurements have corroborated theories¹³ based on chemical investigations of the size of the macromolecule. If these molecules constitute high molecular rings, comparable to double threads, they have a length of about 2000 Å. U. If they are simple long thread-like molecules, they have a length

of about 4000 Å. U., in which case they would attain in one dimension the wavelength of visible light.

Notes

¹ See 18th communication, which precedes.

² Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

³ The theory of Fikentscher and Mark (*Kautschuk*, 1930, 2), which ascribes a spiral form to the rubber molecule, is to be treated elsewhere.

⁴ Cf. Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

⁵ Although the constants vary little, the values may be considered as preliminary ones. In the case of the semi-colloidal cyclo-rubbers, which have been investigated in large numbers, the constant is somewhat smaller, but these molecules have not the same structure as the rubber molecules.

⁶ Staudinger and Bondy, *Ann.*, **468**, 1 (1929); Staudinger, *Kautschuk*, No. 6, 1929.

⁷ Herz, *Z. Elektrochem.*, **23**, 24 (1917).

⁸ Caspari, *J. Chem. Soc.*, **105**, 2639 (1914); *Chem. Zentr.*, **1**, 1194 (1914).

⁹ Pummerer, *Ber.*, **60**, 2167 (1927).

¹⁰ Kröpelin and Brumshagen, *Ibid.*, **61**, 2441 (1928).

¹¹ Meyer and Mark, *Ibid.*, **61**, 1947 (1928).

¹² Ostwald, *Kolloid-Z.*, **49**, 60 (1929).

¹³ Staudinger and Fritsch, *Helv. Chim. Acta*, **5**, 787 (1922).